

STUDY OF METAL LIGAND EQUILIBRIA BY IONOPHORETIC TECHNIQUE



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Under the Supervision of

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M.Sc.

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Certificate of Supervisor

Certified that the thesis on the topic "Study of Metal Ligand Equilibria By Ionophoretic Technique" is the work of Suman Singh, of the Department of Chemistry under my supervision. Her work is original and has completed all the requirements for submitting the thesis for the D.Phil Degree of the University of Allahabad, Allahabad-211002 (INDIA).

Date : 23/7/04

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GLOSSARY AND ABBREVIATIONS

f	Mole Fraction
U	Overall Mobility
u_0	Mobility of Uncomplexed Metal Ion
u_1, u_2	Mobility of Metal Complexes
H^+	Proton and Hydrogen Ion
H_pL	Ligand Associated with Proton
k	Dissociation Constant of Acids
K	Stability Constant of Metal Complexes
β	Overall Stability Constant
$K \begin{matrix} \nearrow^{M-L} \\ \searrow_{M-L-L'} \end{matrix}$	Stability Constant of Mixed Complexes.
L	Ligand Associated with all Ionizable Ion
M	Metal
NTA	Nitrilotriacetic Acid
Σ	Summation of all the terms substituting all values of n
[]	Concentration
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CHAPTER - I

PREFATORY NOTES

PREFATORY NOTES

Coordination Chemistry has been brought up as a very significant branch of Modern Inorganic Chemistry (39) in last few decades. After the Werner's work on the complexes, studies on the coordination compounds were accelerated by the end of 19th century. When the seeds of coordination compounds were germinating, it was investigated as purely inorganic materials. In the second half of 19th century, especially after 1940 the work has regained momentum after slow pace of the foundation. Since then a milestone work has been done in the field of coordination chemistry. The study of coordination compound has now started giving flying colours after much advancement in scope and has included organic chemistry, biochemistry and other areas. A comprehensive survey in this field shows that several reviews and monographs (3, 4, 34, 65, 67) appeared during the first half of 20th century.

Studies in the field of coordination chemistry in the solid state and in solution have grasped the attention of workers. Initially this field consisted of isolation and identification of the complexes in the solid state. In solution the investigations have been carried out from both the thermodynamic and the kinetic point of view. Special attention has been paid towards the solubility of complex species formed in solution.

Bodlander et-al (11, 12, 13) gave birth to the possibility of the determination of stability of the complex species in solution and also about their composition. Niels Bjerrum's (7) dissertation on stepwise formation of complex in 1975 offered a renewed impetus to the problem of stability constants of complexes. The classical work of Jannik Bjerrum (8) on Cu(II)-ammine complexes and Moller's (55) investigation of Fe(III)-thiocyanate complexes failed to, glue the attention of workers to step wise formation of the complex. Research in the aforementioned field gained

momentum after the publication of J. Bjerrum's monograph (9) and the work of Leden (45) in 1941. The subsequent edition of collected work was supplemented by I.U.P.A.C. covering from 1942 to 1947 (49, 65, 70) reveal increasing interest in this field.

PHYSICO-CHEMICAL TECHNIQUES FOR THE STUDY OF METAL COMPLEXES

Gems of physio-chemical techniques are available for the study of complexation reaction. Colligative properties like cryoscopy, vapour pressure, ebullioscopy, molecular volume were initial tools in the determination of metal-ligand interaction. Later on solubility, liquid-liquid partition, surface tension, ion exchange and viscosity methods came in vogue. Among the electrometric method conductometry, potentiometry and polarography have been used. Dielectric polarization, magnetic susceptibility, ultrasonic absorption, enthalpy measurement etc. have found some use in these studies. I.R., Raman and absorption spectroscopy are the main optical method to investigate complexation reactions. In specific cases, other techniques like gas chromatography, optical rotation, N.M.R., light scattering, centrifugation measurements etc. based on reaction rates, biological indication including enzymatic methods have been used.

The process has been proved to be the most important tool in identification of anionic or cationic nature of complex ion (19). Electrophoretic phenomenon has also been employed in the study of the metal-ligand equilibria through gels and determination of transport number for this purpose. Masson (48) Whetham (80) and Steele (75) investigated electrophoresis in gels. Hittorff's (28) study on transport of ions gave an identification of complex ion formation. Chelates of Mg with oxalate and citrate were prepared by Monnier and Choteau (55) and quantitative information about their stabilities were studied by paper electrophoresis. Leblanc and Noyes (44) in 1890, provided the information of cyano argentate anion with the help of electrophoretic experiments.

Mcdonald and Coworkers (50, 51, 52) discussed the factors that influence the ionographic mobility of a migrant. They have discussed the

various factor which effects the movement of a charged species on paper strips under a potential gradient. Their results tallied with the literature values available at that time. The paper fibers according to them, act as a barrier to the motion of charged species. Their effect depend upon the molecular volume, shape and charge of migrant in the electro-osmosis. The paper strip in solution generally bears a negative charge consequently, the movement of the ion is effected.

Kunkel (41) and Tiselius (77) found acceptable value of migration with the help of several experiments. The work of Kunkel appears to be more authoritative in respect of measurement of mobility and stability. He suggested that the correct value of mobility can be obtained if electrophoretic correction factor is accounted. This correction factor can be obtained by using dextrose as an indicator of electro-osmosis movement. Further Kunkel and Tiselius have sponsored the view that the ion while moving has to move through hedges of obstacles on the surface of the paper. It's path length is not the same as the length of the paper strip and this decreases the actual motivating potential gradient. Lahiri et al (42, 43) used glucose instead of dextrose as an indicator.

Till 1960's not much work appears to be on record on the application of electrophoretic technique for the investigation of metal complexes. In 1964, Jokl (31) laid the foundation stone in the determination of stability constants of metal ligand systems in solutions. He carried out electromigration studies of amino-acid complexes of several bivalent metals and also determined the stability constants of those metal complexes. The stability constants were determined by plotting the migration velocity against the logarithm of ligand concentrations by suitable treatment. Biernat (6) devised a theoretical treatment similar to that of Jokl for the study of successive complex formation in solution. Using paper electrophoresis, Dey and Coworkers (18) have studied various complexes of Cu(II) and Fe(III).

Hurnik (30) followed the footsteps of Jokl and Biernat and studied the formation of tartarate complexes of Fe(III), Co(II) and Ni(II) in aqueous medium and determined their stability constants. Li Changhua et-al (46) used a new graphical method for determining the composition of complexes and formation constant by spectrometric method. Koch (36) studied oxalate and succinate complex of Tl (I) whereas investigations on the Cu(II), Co(II), Ni(II), Cd(II), Zn(II) and Mg(II) complexes of malonic acid and its alkyl derivatives was done by Kozak (40). Soni and Bartusek (73) investigated Mo(II) complexes of o-diphenyl and compared the stability constants with those obtained by spectrophotometric method.

The testimony for the binary and ternary formation constant of mixed amino acid complexes with Zn(II), Cu(II), Ni(II) and Cd(II) potentiometrically was coined by Huang et-al (29). Tsventanova et-al (78) obtained 1:1 and 1:2 Cu(II) ligand complexes and investigated the stability constants of Cu(II) with acid hydrazines. Neves and Coworkers (59) have studied the mixed ligand complexes of Cu(II) with pyridine. Prisyazhnyuk et-al (62) studied the effect of carboxylate anion in complexation of Co(II) with phenyl hydrazine. Shemyakina (68) studied the formation and stability of Cu(II) complexes with α -amino acid anions and amino carboxylic groups of collagen of native fibril, pH- metrically at 298K. In the formed Cu(II) complex, copper binds to the amino carboxylate groups of the proteins and to the nitrogen atoms and carboxylic groups of amino acid. Structures are proposed for these complexes and their stability constants and the influence of the nature of the amino acid on stability are determined. Goina et-al (26) studied the formation constants of the complexes of Cu(II) glutamate system by spectrophotometric and potentiometric methods.

Kabaeva and Coworker's (35) have determined the stability constant of tris (2, 2'-bipyridine) Nickel (II) thiocyanate complexes. Li, Yuhu (47) gave evidences for calculation of molar absorptivity and apparent constant

of stability of the colour complex by parameter optimization method and discovered that the apparent stability constant was markedly influenced by molar absorptivity. Nepal and Dubey (58) studied the stability of quaternary complexes of Co(II), Ni(II) and Cu(II) ions by paper electrophoresis. Thermodynamic parameters for the protonation of carboxylic acid in aqueous tetraethyl ammonium iodide solution were analysed by De, Roberties et al (17).

The binary and ternary formation constants of mixed amino-acid complexes with Zn(II), Cu(II), Ni(II) and Cd(II) were potentiometrically determined by Huang Zhongxian et-al (29). It is expected that the ternary amino-acid complexes are overwhelmingly distribution specially at biological conditions. Aleman et-al (2) investigated the coordination system Cu(II)-neutral L-isoleucine and Cu(II)-L-isoleucinate ion were studied by polarographic method in aqueous medium at $\mu=0.1M(NaClO_4)$ and $25 \pm 0.1^\circ C$ and the stability constant of the complexes formed were determined.

Stability constant were determined pH-metrically for Cu(II), Mn(II), Ni(II) and Zn(II) complexes with serotonin creatinine sulphate by Fedorchuk et al (22). These metals form 1:1 and 1:2 metal ligand complexes.

Wasylikiewicz, Stanislaw (79) gave a mathematical model of aqueous solution of weak electrolytes. Anion and cations association in the aqueous solution of bivalent metal sulphates forming ion pairs, which are molecular solution (no charge species), the same pitzer model of strong electrolytes was extended to take into account ion-molecule and molecule-molecule interactions. The thermodynamic stability constants of ion pairs and the other parameters of the model of aqueous solution of bivalent metal sulphates ($CuSO_4$, $CoSO_4$, $NiSO_4$ and $ZnSO_4$) were estimated on the basis of spectrophotometric and activity coefficient data.

Nadia and Coworkers (57) studied the solution spectra of Fe(III) complex with aspartic acid and glutamic acid mono hydroxamates in the UV-Vis region for different complex species in the pH range 1.0-4.0 at ionic strength 0.15M NaCl and 25°C.

The stability constant of the ternary complexes of Fe(III), Cu(II), Ni(II) and Co(II) using serine as primary ligand and leucine as secondary ligand have been studied by Sameena et-al (66) with the help of ionophoretic technique at $\mu=0.1\text{M}$ and 25°C. They have also investigated the ternary complexes of the same metals using leucine/serine as a primary ligand and NTA as a secondary ligand.

R.K.P. Singh (71) study the stability constant of norvaline complexes of Cu(II), Ni(II) and Co(II) by ionophoretic technique. Patel et-al (61) investigated the ternary complexes of Fe(III), Cu(II), Ni(II) and Co(II) using salicylic acid as a primary ligand and NTA as a secondary ligand by ionophoretic technique at $\mu=0.1\text{M}$ and 25°C.

In most of the cases, the investigations are only quantitative and not much eagle eyed attention has been paid for the step wise formation of complexes. In the present work ionophoretic technique has been employed to study the metal-ligand equilibria in solution.

IONOPHORESIS

The word Ionophoresis depict the separation of charged molecular species on the basis of their movement under the influence of an applied electrical field where positively charged ions moves towards the cathode, and negatively charged ions move towards the anode. A. Tiselius (77) was the first person to give birth to the technique of electrophoresis. His play ground of work was chemistry of serum protein and the research led to the development of specialized apparatus and methodology that has proved to be of great utility and in 1948 he was awarded with Noble prize for his poineer work in this field.

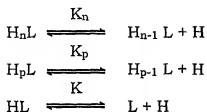
In 1907, Field and Teageu (23) studied the electromigration of diphtheria toxin with antitoxin in agar jelly. Many other workers like Jones (33), Duclaux (20), Boutraic (14) and Enslin (21) have employed the above technique, and obtained fruitful results. Paper electrophoresis was first brought into use by Koning (37) in 1937, although Kapaczewspi (38) has earlier noted the electro capillary phenomenon of several anions and cations. Collidge (15) managed to seperate protein in a column packed with glass wool under the influence of an electrical field. Strain (74) was the first to report the combination of electrophoresis with chromatographic adsorption in conventional Tswett column filled with cotton. The technique of paper electrophoresis was used to separate the inorganic ions in a number of laboratories without much modification (10). For separation of amino-acids utilizing this technique, a number of reviews have appeared in the period between 1948-1953 notably by Tiselius (77), Albert (1), Friche (24) and Widemann (82) and considerable advances have been made in the technique and separation of charged particles. Remarkable reviews on paper electrophoresis are available especially by Winderly (83), Hans and Mc. Donald (27), Berlingozzi (5), Munier (56) and Michalic (53).

In the words of Glasstone (25) little work has been done on the transference of ions in mixtures although both Hittorff and Moving boundary methods have been employed. It is possible to derive the required transference numbers by the analysis of anode and cathode compartments before and after electrolysis. Though in our laboratory various investigations (17, 76, 53, 60) have been done, the present work is based on the above idea of transference number and has been evolved which can be Titled as "Solution Electrophoresis" or "Ionophoresis".

THEORETICAL

The technique used in these studies is Electrophoretic technique which consists of examining the rate of movement of metal ions in a mixture containing ligand solution under a definite potential gradient in a tube. It is measured at different pH's of the mixture solution.

A ligand may be assumed to be a polybasic acid dissociating in stages as follows:



(Charges have been ignored)

The concentration of a protonated species H_pL can be expressed as

$$\begin{aligned} [H_pL] &= K_p [H_{p-1}L] [H] = K_p \cdot K_{p-1} \cdots K_1 [L] [H]^p \\ &= \alpha_p [H]^p [L] \end{aligned} \quad \text{-----(1)}$$

Where $\alpha_p = K_1 \cdot K_2 \cdots K_p$

The polybasic acid thus distributes itself in the form of different anionic species.

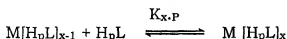
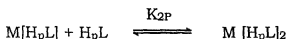
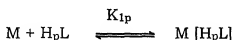
The following expression holds good for the total concentration.

$$T_A = \sum_{p=0} \alpha_p [H]^p [L]$$

In view of this expression equation (1) becomes

$$[H_pL] = \frac{T_A \alpha_p [H]^p}{\sum_{p=0} \alpha_p [H]^p} \quad \text{-----(2)}$$

A metal ion M may complex with any deprotonated species of acid and the reaction can be expressed in a general way as (charges being ignored):



The concentration of a general complex species H_pL can be expressed as:

$$\begin{aligned} [M(H_pL)_x] &= K_{xp} [M(H_pL)_{x-1}] [H_pL] \\ &= K_{xp} K_{x-1p} \dots K_{1p} [H_pL] [M] \\ &= \beta_{xp} [H_pL]^x [M] \end{aligned} \quad \text{-----}(3)$$

Where $\beta_{x,p}$ is overall stability constant of the complex and is given by the expression;

$$\beta_{x,p} = K_{1p} \cdot K_{2p} \dots K_{xp} \quad \text{-----}(4)$$

The pH of the aliquot determines the relative abundance of a particular anionic species of the polybasic acid. The metal ion in solution forms a variety of complexes with these anionic species of the polybasic acid depending upon their stability constant as well as the availability of the different anionic species.

Under the influence of electric field imposed on the ends of electrophoretic tube the complex formed move, whose speed under the unit potential gradient can be given by popular equation of Jokl (32)

$$U = \sum u_{x,p} f_{xp} \quad \text{-----}(5)$$

Where $u_{x,p}$ is the speed and f_{xp} is the mole fraction of a general complex $M[H_pL]_x$ present in the conglomeration.

It is noteworthy, that the general formula (5) clearly accounts for the stability of each species of complex in view of variability of x and p from zero to any integral number. The mole fraction $f_{x,p}$ intrinsically stand for the actual fraction constituted by the particular complex species in total conglomeration of all the complexes formed in the interaction of the metal ion with anionic species of the ligating polybasic acid present in the solution under the specific conditions of acidity obviously.

$$f_{x,p} = \frac{[M(H_p L)_x]}{\sum [M(H_p L)_x]}$$

This expression in view of equation (3) Simplifies to;

$$f_{x,p} = \frac{\beta_{x,p} [H_p L]^x}{\sum \beta_{x,p} [H_p L]^x}$$

Now equation (5) may be expressed as :

$$U = \frac{\sum u_{x,p} \beta_{x,p} [H_p L]^x}{\sum \beta_{x,p} [H_p L]^x} \quad \text{-----(6)}$$

This equation is a general expression correlating the overall mobility 'U' with the mobility $u_{x,p}$ of the individual complexes present in the solution and as well as with their relative abundances. To be concrete if partially unprotonated and protonated species are considered. The equations (6) can be expressed as :

$$U = \frac{u_{0,0} \beta_{0,0} + u_{1,0} \beta_{1,0} L + u_{2,0} \beta_{2,0} [L]^2 + \text{-----} u_{1,1} \beta_{1,1} [HL] + u_{2,1} \beta_{2,1} [H_2L]^2 + \text{-----}}{\beta_{0,0} [L] + \beta_{1,0} [L] + \beta_{2,0} [L]^2 + \beta_{1,1} [HL] + \beta_{2,1} [HL]^2 + \beta_{2,2} [HL]^2 + \beta_{1,2} [H_2L] + \text{-----} \beta_{2,2} [H_2L]^2 + \text{-----}}$$

In the above expression $\beta_{0,0} = 1$ in view of expression (3). $u_{0,0}$ is the speed of uncomplexed metal ion $u_{1,0}$ is that of the complex formed by the exact combination of one deprotonated anionic ligand with the metal ion and $u_{x,p}$ is the speed of metal complex formed by the combination of x anions containing p protons each.

The overall stability constants of the different metal complexes formed in interaction are denoted by β 's, Jokl's is different from this equation in the manner as much as it comprehends different mononuclear complexes formed with a particular liganding anionic species. As the experiments are comprised of recording the speed of the metal ion with advancing increase of pH due to addition of hydroxyl ion (sodium hydroxide solution) the overall average speed would gradually change because of change in relative abundance of a particular species obviously depends upon its overall stability constant as well as on the availability of the particular liganding ionic species in the solution which in turn depends on the acidity status of the solution, therefore they all are interrelated.

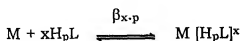
Electrophoretic tube is the basis of all the studied done earlier. 10 ml aliquot having metal ion and ligand were taken in tube and then electrolysed. The ions or complexes present in the solution move towards the respective electrodes relying upon the charges present on them. At a low pH the minimum concentration of a metal ions (bivalent and trivalent cations) move toward the cathode leaving lesser amount of metal ion in unelectrolysed condition. Singh et-al (70) have established the relation between the mobility of metal ion and it's concentration in the cathodic compartment. As the pH of the solution was increased the complexation took place and depending upon the charge on the complex the concentration of metal ion increases simultaneously. Colorimeter was used to measure the concentration of metal ion by taking absorbance. At low concentration range absorbance is proportional to concentration. By measuring the absorbance of unelectrolysed solution and that of electrolysed solution of the same compartment, difference in absorbance was calculated and a graph was drawn between pH and absorbance difference ($A_0 - A$). This would give a curve where in a number of plateaus occur. Each plateau corresponds to a region where a particular metal complex predominates over others. The stretch of the plateaus will be long

if the stability constant of the relevant metal complex is large as compared to that of neighbouring complexes.

Experimentally, it was determined that mobility of the ion bore a reciprocal relation to the difference of absorbance.

The stability constants of different complexes can be calculated with the help of equation (6) and it's graphical representation of absorbance difference 'A₀-A' related to pH values of the solution. In the rudimentary studies the hydrogen ion concentration is very high (i.e. low pH value). The overall mobility of metal ion would be chiefly due to uncomplexed metal ion. Thus the first plateau would correspond to the region where metal ion is practically uncomplexed. Beyond this region at higher pH the overall migration of metal ion falls gradually due to increasing complexation of metal ion with acid anion. This fall persists till a stage is reached where almost all metal ions are complexed with the liganding ion with the result that the overall mobility would tend to become constant on this region of plateau. This persists as long as the formation of the complex overwhelmingly dominates. It is thus seen that when an ionic species remain predominant in a region of pH the absorbance also remains the same showing a constant region in the plateau. In the region, between the two plateau's, the overall mobility would be contributed by the mobilities of the uncomplexed metal ion and first complex of metal ion with the particular anion of the ligand.

Assuming the H_pL anion of the liganding acid to have preferentially formed the complex with the metal ion as:



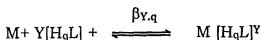
In the earlier stages the equation (6) simplifies to :

$$U = \frac{u_{0.0} + u_{x,p} \beta_{x,p} [H_pL]^x}{1 + \beta_{x,p} [H_pL]^x}$$

The other terms in the numerator and denominator of this expression have been justifiably ignored because of the negligible formation of other complexes in this region. From this simplified equation it is easy to calculate the overall stability constant ($\beta_{x,p}$) for the first formed complex $M(HpL)^x$. The overall mobility would be equal to the average mobility of $u_{0,0}$ and $u_{x,p}$ (these are the mobility corresponding to the first and second plateaus), when $\beta_{x,p}[HpL]^x$ is equal to one. The pH value on this condition is found out by taking the mean value of the two plateaus and by the knowledge of different dissociation constants of the ligand the concentration of HpL variety can be calculated at this pH with the help of the equation (2). The reciprocal of the concentration gives the overall stability constant $\beta_{x,p}$.

On further increasing the pH value of the solution, other anionic species of the ligand are increasingly formed at the cost of the more deprotonated ones. This would lead to the formation of a new complex. Now the absorbance difference which was constant at the second plateau will steadily suffer a transition till a stage is reached where a new complex is overwhelmingly formed. The absorbance difference remains constant as long as the new complex is in dominant majority.

Assuming HqL to be the new anionic species of the ligand to be preferentially generated in the system, on increasing its pH, from the second plateau onwards, its complexation with the metal ion would be :



The overall mobility in the region between the second and third plateau may be given by following expression:

$$U = \frac{u_{x,p} \beta_{x,p} [HpL]^x + u_{Y,q} \beta_{Y,q} [HqL]^Y}{\beta_{x,p} [HpL]^x + \beta_{Y,q} [HqL]^Y}$$

A number of terms in the numerator and denominator have been deleted because of obvious reason of their insignificant contribution. $u_{Y,q}$

is obviously the mobility of the newly formed complex which corresponds to the third plateau.

Applying the earlier technique, the average of the two mobilities $u_{x,p}$ and $u_{y,p}$ would be overall mobility at a point where,

$$\frac{\beta_{y,q} [H_qL]^y}{\beta_{x,p} [H_pL]^x} = 1$$

The pH of the system at this point was calculated by taking the mean point of the slop and the concentration of H_pL and H_qL can be calculated by considering equation (2). Knowledge of these values and that of $\beta_{x,p}$, we can calculate the overall stability constant $\beta_{y,q}$ of the other complex $M[H_qL]^y$. So we are able to calculate stability constant of any complex formed subsequently with the help of this method.

EXPERIMENTAL

I. INSTRUMENTS

1. Electrophoretic tube
2. Electrodes
3. pH-Meter and Accessories
4. Electrophoresis Power Supply
5. Spectro-Colorimeter.
6. Thermostatic Water Bath
7. Ionophoresis Set-Up

II. CHEMICALS

1. Metal Solution (Fe(III)/Cu(II)/Ni(II)/Co(II))
2. Standardization of Metal ion Solutions.
3. Ligand Solutions
4. Background Electrolyte
5. Developing Reagents of Fe(III)/Cu(II)/Ni(II)/Co(II)

INSTRUMENTS

ELECTROPHORETIC TUBE :

A simple electrophoretic glass tube has been designed for this work which, after standardization yields remarkable results. The tube is 18 cm long and 5mm bore with a stopper in middle and is fused perpendicularly at the ends with short wider tubes of 1.2cm internal diameter. These side arms have been utilized to insert the electrodes. The tube has been marked in such a way that it contains aliquot's of 10ml.

While performing experiments this tube is kept in a thermostatic water bath. The position of the tube was adjusted in such a way that the level of the solution in one wide arm reaches the circular mark on it. This adjustment fixes the equal volume of the solution on both sides of middle stopper.

ELECTRODES :

Simple glass platinum electrodes are fabricated and used in experiments. A $0.5 \times 0.5 \text{ cm}^2$ platinum strip is fused at terminal end of glass rod and connected to electrophoretic power supply through mercury copper wire connection.

pH METER AND ACCESSORIES :

A digital pH Meter, century Digital (Model OP-901) was used. The pH-Meter works with single glass electrode. A stabilized AC main at 220V/50Hz was used for pH-meter.

ELECTROPHORETIC POWER SUPPLY :

A constant voltage electrophoresis power supply of SYSTRONICS (Model 604 PE) was used. The power supply has a rating of 0-300 volt DC in three different ranges Viz. 0-100, 100-200 and 200-300. For this work a constant potential difference of 50 Volt DC was used from this power

supply. The main AC supply was stabilized using a constant voltage transformer.

SPECTRO-COLORIMETER :

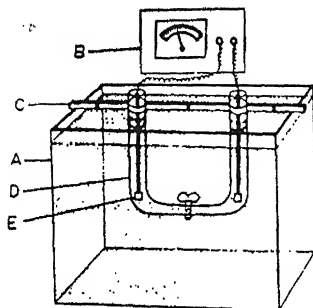
A colorimeter of visible spectrum rang (400-750nm) of CARL-ZEISS (JENA) Model SPECOL has been used. This instrument displays minimum absorbance at 0.005 (least count).

THERMOSTATIC WATER BATH :

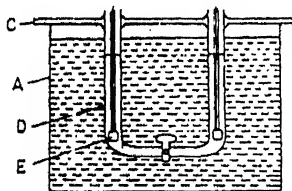
A SICO made constant temperature water bath has been used. To ensure uniform temperature speed regulated stirrer was used.

IONOPHORESIS SET-UP

SURFACE VIEW



DIGRAMMATIC



- A- Water bath
- B- Electrophoresis supply
- C- Support
- D- Ionophoretic tube
- E- Pt Electrodes

CHEMICALS

WATER :

Distilled water was redistilled over alkaline permanganate. The resultant distilled water was cooled in well stoppered pyrex flask. This was used for preparing solutions over the period of investigations.

METAL SOLUTIONS :

Solution of metal perchlorates were prepared by the first precipitation of metal carbonate from 0.1M solution of sulphates of Cu(II), Ni(II), Co(II) with solution of sodium carbonate (chemically pure grade) except Fe(III) and then, precipitate were thoroughly washed with water and treated with A.R. grade perchloric acid. These are boiled on a water bath and filtered to get stock solution of the metal perchlorate $1.0 \times 10^{-2} \text{M}$ (approx). The concentration of metal ion solution was kept low (10^{-3}M) to avoid the formation of dimeric, hydroxo metal-metal ion complex in water.

Stock solution of Fe(III) was prepared by oxidising standard Ferrous ammonium sulphate solution with nitric acid. The excess of acid was boiled off. The final concentration of Fe(III) solution was kept to 10^{-4} .

STANDARDIZATION OF METAL ION SOLUTION

(I) Cu(II) PERCHLORATE :

10ml of Cu(II) perchlorates were taken in sintered vessel and the murexide indicator was added to it. A buffer solution of pH 10.0 was then added dropwise till the colour of the solution changes to yellow and the initially formed precipitate was redissolved. The solution was then diluted to 100ml with distilled water and it was titrated against a standard EDTA solution till the colour change from yellow to deep blue.

(2) Ni(II) PERCHLORATE :

10ml of Ni(II) perchlorate solution, 5ml of buffer of pH 10 and murexide indicator were added in a titration vessel. The resulting mixture was then titrated against standard EDTA solution till the colour change from yellow to deep violet.

(3) Co(II) PERCHLORATE :

Co(II) perchlorate solution was taken in a conical vessel to which standard EDTA solution was added in known excess and then 5ml of buffer of pH 5 and 3-5 drop of 1-(2-phridylaxo)-2-Naphthol (PAN indicator). The solution was diluted to 60ml. The unused EDTA was titrated against standard Co(II) perchlorate solution until the colour of solution changes first to violet. A few drops of EDTA solution were added to restore yellow colour. The amount of Co(II) was known by the amount of EDTA consumed by it.

BUFFER SOLUTION :

A buffer solution of pH 4 and pH 9 were prepared by each dissolving one buffer tablet of pH 4 and pH 9 in distilled water and then making up the volume to 100ml by distilled water.

SOLUTION OF THE COMPLEXING REAGENTS:

Stock solution of the complexing ligands viz. Benzoic Acid, 2-Chlorobenzoic Acid and 4-Hydroxybenzoic Acid were prepared by dissolving accurate weighed proportion in water. By dilution solutions of required strengths were then prepared.

PERCHLORIC ACID AS BACKGROUND ELECTROLYTE :

A stock solution (1.0M) was prepared by suitable dilution of 70% perchloric acid. The solution was standardized by titrating a suitable volume of its dilute solution against a standard sodium hydroxide solution.

DEVELOPING REAGENTS FOR Cu(II)

(i) POTASSIUM PERSULPHATE SOLUTION :

A saturated solution of potassium persulphate was prepared by dissolving excess of the reagent in distilled water. The supernate thus obtained was used as a developer.

(ii) AMMONIUM THIOCYANATE SOLUTION :

A 50% solution of ammonium thiocyanate of A.R. grade reagent was prepared by dissolving 50gms of the reagent in 100ml measuring flask.

Acetone : GR grade

Concentrated HCl, AR grade.

DEVELOPING REAGENTS FOR Ni(II)

(i) SATURATED BROMINE WATER :

Approx 4gms or 1ml of pure bromine (AR grade) was added carefully to 100ml of distilled water. A slight excess of undissolved bromine is left at the bottom of mixture.

(ii) CONCENTRATED AMMONIA SOLUTION :

Concentrated ammonia solution was prepared by doubly diluting the liquor ammonia solution (stock).

(iii) DIMETHYLGLYOXIME REAGENT :

0.1% of dimethylglyoxime reagent was prepared by dissolving 0.1gms of the reagent in 20ml absolute alcohol in 100ml measuring flask.

DEVELOPING REAGENTS FOR Co(II) :

STANNOUS CHLORIDE SOLUTION :

20gms of SnCl_2 (GR grade) was dissolved in 40ml of concentrated HCl in a 100ml measuring flask then the solution was made upto the mark by adding distilled water.

AMMONIUM THIOCYANATE SOLUTION :

A 50% solution of ammonium thiocyanate solution was prepared by dissolving 50gms of reagent in distilled water in 100ml measuring flask.

DEVELOPING REAGENT FOR Fe(III):

AMMONIUM THIOCYANATE :

A 20% solution was prepared by dissolving 20gms of AR grade ammonium thiocyanate in 100ml distilled water.

PROCEDURE OF COLOUR DEVELOPMENT OF DIFFERENT METAL IONS

Cu(II) Ion :

The electrolysed solution of anodic compartment was taken in a 15ml flask. To the electrolysed solution 0.6ml of Conc. HCl proceeded by 0.15ml of saturated ammonium peroxydisulphate solution. Then a mixture of 0.75ml of 50% ammonium thiocyanate and 7.5ml of acetone was added. The volume was made upto the mark and the absorbance was taken at $\lambda_{\max} = 408\text{nm}$ against a reagent blank, within five minutes of mixing of the reagents.

Temperature was kept below 10°C and better results were found when temperature was kept at 5°C. At this temperature complex is quite stable and if reading were taken within five minutes then the results were found to be best.

The copper thiocyanate colour fades rapidly from auto reduction unless an appropriate holiday oxidant is present. Since peroxydisulphate does not interfere with the reagents, so it was used. Copper thiocyanate shows greater colour intensity with acetone hence it was used not as a solvent but as a colour intensifier (67).

Ni(II) Ion :

The electrolysed solution of the anodic compartment was taken in a 15ml flask. To this solution 0.6ml of saturated bromine water was added

proceeded by 1.2ml of liquid ammonia solution. Then 0.6ml of 1% dimethyl glyoxime was added and mixed thoroughly. Absorbance was taken against a reagent blank at 445nm. The temperature should not exceed 30°C. Readings were very accurate when taken after five minutes of mixing and before ten minutes. The bromine water oxidises nickel ion to a higher oxidation state probably Ni(III) and Ni(IV) since the complex nickel dimethyl glyoximate is formed at higher pH. So an excess of ammonia water was added after bromine water.

Co(II) Ion :

The electrolysed solution of anodic compartment was taken in a 15ml flask. To this solution 1.5ml of stannous chloride (20%) was added. Then a mixture of 0.75ml of 50% aqueous ammonium thiocyanate solution and 7.5ml of acetone was added to it. It was mixed and blue coloured solution was obtained. The volume was made up to the mark. The absorbance was taken at 625nm against a reagent blank. The blue colour of Cobalt thiocyanate becomes intensified by the addition of acetone, so it was used as a colour intensifier.

Fe(III) Ion :

The electrolysed solution of the anodic compartment was taken in a 15ml flask. To this solution 1ml perchlorate solution was added. The volume was raised upto the mark and then the absorbance of Fe(III) thiocyanate complex was measured at 480nm against a reagent blank (72).

IONOPHORETIC TECHNIQUE IN THE STUDY OF BINARY COMPLEXES

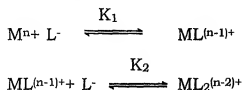
Ionophoretic technique for investigation of binary complexes includes the study of the nature and stability constant of Benzoic Acid, 2-Chlorobenzoic Acid and 4-Hydroxybenzoic Acid as complexing ligands with the metal ions viz, Fe(III), Cu(II), Ni(II) and Co(II).

It was found that the absorbance by the Cu(II), Ni(II), Co(II) and Fe(III) with different complexing agents obey Beer's law in the relevant concentration ranges of the metal ion used in the ionophoretic studies and the presence of the complexing agents does not interfere in the absorbance measurements.

The observed mobility of migrating cation was calculated by measuring the change in the absorbance of the solution contained in anodic compartment. First the 10ml aliquot was taken in the electrophoretic tube and after adjusting the mark the stopper was closed. The solution of the compartment was taken out in a 15ml flask and then it was developed as described, and its absorbance was measured. This was A_0 i.e. absorbance without electrolysis.

Then again, an aliquot of 10ml of the same composition was taken at different pH in the electrophoretic tube. After electrolysis this mixture at 50V potential difference for 45 minute the middle stopper was closed. The electrolysed solution of anodic compartment was taken in a 15ml flask and again after developing its absorbance was taken. This was A i.e. the absorbance after electrolysis. The difference between the two absorbance value give the mobility of the respective ion.

Under a potential gradient a metal ion will move in the field. The speed and its direction depends upon the charge and size of the metal ion. Assuming the metal ion to have ligated with a ligand to give complexes as:



It is obvious that free metal ion, $ML^{(n-1)+}$ and $ML_2^{(n-2)+}$ complex constitute

$$\frac{1}{1 + K_1 [L] + K_1 K_2 [L]^2}, \quad \frac{K_1 L}{1 + K_1 [L] + K_1 K_2 [L]^2} \text{ and } \frac{K_1 K_2 [L]^2}{1 + K_1 [L] + K_1 K_2 [L]^2}$$

fractions respectively of the total metal ions in reaction mixture. During the process of electrolysis different ions move in swarm in one direction or the other, hence the environment of any ionic entity remains unchanged in bulk during migration. As such the composition of the metal ion (in free as well as in ligated states) remains intact during the migration.

No doubt the speed of various ionic species of metal ions should be different but the condition of fixed composition at any movement time rules out separation of the species in the bulk. Overall effect of this overriding condition is that metal ion will move with a speeds which is composite of weighted speeds of free and complexed metal ions. The weighting factors be actual fraction of the total metal ion constituted by a particular species. Hence, the overall mobility, 'U' should be given by the following expression as used by various workers. (6, 32)

$$U = f_1 u_1 + f_2 u_2 + f_3 u_3 + \dots$$

Where u_1, u_2, u_3 are the mobilities and f_1, f_2, f_3 are the mole fractions of $M^{n+}, ML^{(n-1)+}$ and $ML_2^{(n-2)+}$ respectively.

If the tube is not uniform, the potential gradient will be different at different places. The resistance of the reaction mixture present in narrower zones of the tube will be greater than an overall resistance which should be constituted of several varying resistance put in series. Obviously, the potential gradient in the narrower zones will be more than

that in the broader zones. It would be certainly inversely proportional to the cross sectional area of the bore of that zone. This would lead to necessary conclusion that the number of ions passing out through any cross sectional area per unit time would be the same regardless of the non uniformity of the tube.

Various factors (e.g. diffusion, temperature, ionic strength) obviously variate the electrophoretic mobility of a particular ion. Diffusion should be significant in the vicinity of the electrodes. A perusal of the literature (63) reveals that the diffusion coefficients of the ions are in the range of $10^{-5}\text{cm}^2 \text{ sec}$ units, which is negligible in comparison to the ionic mobility (10^{-3}cm) therefore the electrophoretic mobilities can not be effected by diffusion. The loss in concentration of the metal ion in anodic compartment from absorbance measurements, should obviously be proportional to the mobility of positively charged metal ion leaving that compartment.

It can be said through observation, that the ratio of the loss in concentration in the anodic compartment and the concentration before electrolysis is constant regardless of the initial concentration of the metal ions. This fact justifies the view point that in the electrolysis process in the tube, the mobility of metal ion is not at all changed by its dilution or non-uniformity of the tube.

IONOPHORITIC TECHNIQUE IN THE STUDY OF MIXED COMPLEXES

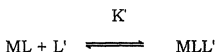
Due to interaction of two different liganding species to a metal ion, mixed complexes are formed. The formation and stability constants of mixed complexes have been investigated by various workers using various techniques as already described in this chapter.

Our laboratories bears the distinction of using ionophoretic technique for the first time for investigation of mixed complexes and determination of their stability constants. Present thesis consist of the study of mixed complexation reactions of metal ions Fe(III), Cu(II), Ni(II) and Co(II) with Benzoic Acid/2-Chlorobenzoic Acid/4-Hydroxybenzoic Acid as primary ligand and Nitrilotriacetic Acid (NTA) as secondary ligand. Discovery of the fact was done that, one NTA molecule coordinates with one metal ion giving a stable complex which is formed in the low pH range and remains stable at higher pH value, with the help of the above described method, their stability constant have been determined.

For the through investigation of the mixed complexation, primary ligand Benzoic Acid/ 2-Chloro Benzoic Acid/ 4-Hydroxy Benzoic Acid are taken in the order of $1 \times 10^{-2}M$ and pH was kept constant at 7.0. The secondary ligand i.e. NTA concentration is increased simultaneously and the difference in the absorbance was noted. Maintenance of pH 7.0 has it own reason. It was deduced from the study of M-ligand and M-NTA system that formation of final complexes in both the system is completed much below of this pH and the stability of the metal complex becomes non variant. Hence electrophoretic investigation on progressive addition of NTA to the solution containing 1×10^{-2} benzoic acid, 2-chlorobenzoic acid and 4-hydroxybenzoic acid was supposed to revel the transition of M-acid system to M-NTA system. It would also give definite indication of a mixed complex if formed in the transition. So on the plot of difference in absorbance against the negative logarithm of concentration of added NTA, a curve is obtained showing two plateaus. It shows that the first plateau

is due to M-acid complex and the second plateau is due to newly formed complex.

This new complex can not be 1:1 or 1:2 M-NTA complex species as the absorbance difference are different from the absorbance difference of this new complex. Since the absorbance difference A_0-A is more negative than the mobility of pure M-NTA complex. It is inferred that the NTA species is coordinated with M-ligand complex forming a more negatively charged complex. The interaction may be represented as:



Where M is metal ion,

L is primary ligand,

L' is secondary ligand (NTA).

Under these conditions overall mobility can be given by expression:

$$U = \frac{u_0 + u_1 K' [L']}{1 + K' [L']}$$

Where u_0 and u_1 are mobilities of M-ligand (acid) and mixed (MLL') complexes respectively. Using again the principle of average point K' can be determined to be equal to $1/[L']$. However the formation of ML i.e. Metal-ligand (acid) complex, the equilibrium $M+L \xrightleftharpoons{K} ML$ holds good where K is stability constants of Metal-ligand complex and can be determined as described earlier.

Form above two chemical equilibria

$$\begin{aligned} MLL' &= K' [ML] [L'] \\ &= KK' [M] [L] [L'] \end{aligned}$$

Obviously KK' is the overall stability constant of mixed ligand and this can be assessed with the knowledge of K and K' i.e.,

$$\beta_{mix} = KK'$$

WORK CARRIED OUT IN THE THESIS

In the attentive work a comprehensive study of the metal-ligand interactions using Ionophoresis has been brought up. The studies of the following systems are described in the subsequent chapters.

1. Metal - Benzoic Acid
2. Metal - 2-Chlorobenzoic Acid
3. Metal - 4-Hydroxybenzoic Acid

Where metal ions are Fe(III)/Cu(II)/Ni(II)/Co(II)

The attentive work also includes the study of ternary complexes involving NTA as a secondary ligand. The ternary system studies include-

1. Fe(III)-Benzoic Acid/2-Chlorobenzoic Acid/4-Hydroxybenzoic Acid - NTA
2. Cu(II)-Benzoic Acid/2-Chlorobenzoic Acid/4-Hydroxybenzoic Acid - NTA
3. Ni(II)-Benzoic Acid/2-Chlorobenzoic Acid/4-Hydroxybenzoic Acid - NTA
4. Co(II)-Benzoic Acid/2-Chlorobenzoic Acid/4-Hydroxybenzoic Acid - NTA

Experimental observations concerning the above binary and ternary systems are described in the various chapter II, III respectively and an attempt has been made to interpret them in chapter IV. The stability constants of binary and ternary complexes have also been determined.

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CHAPTER - II

STUDY OF BINARY COMPLEXES

STUDY OF BINARY COMPLEXES

The present chapter includes the study of the nature and stability constant of Benzoic acid, 2-Chlorobenzoic Acid and 4-Hydroxybenzoic Acid as complexing ligands with the metal ion viz Fe(III), Cu(II), Ni(II) and Co(II).

EXPERIMENTAL PROCEDURE :

The solution containing $1 \times 10^{-2}M$ and $1 \times 10^{-3}M$ (for Fe(III) only) ligand solution (Benzoic Acid, 2-Chlorobenzoic Acid, 4-Hydroxybenzoic Acid), 0.1M perchloric acid solution and respective amount of metal ion solution $1.0 \times 10^{-3}M$ Cu(II), Ni(II), Co(II) and $1.0 \times 10^{-4}M$ Fe(III) were prepared respectively. The pH of the solution was adjusted by adding NaOH solution.

10ml one of this aliquot was taken in an electrophoretic tube and then thermostated at $25^{\circ}C$. The position of the tube is so adjusted that the level of the solution in one wide end arm reaches a circular mark on it. This adjustment fixed the volume on either side of the middle stopper. The arms of the tube are then marked as cathodic and anodic compartments. Two $0.5 \times 0.5cm^2$ platinum electrodes were dipped in each arm cup. The electrodes were then connected to electrophoretic power supply, cathode electrode to negative and anodic electrode to positive supply. A potential difference of 50 Volts was applied between electrodes and middle stopper was left open. After 45 minutes the middle stopper was closed, power supply turned off and electrodes are withdrawn. There after the solution of anodic compartment was taken in a 15ml measuring flask. The specific developing reagents for different metal ions were then added to make up the volume to 15ml. The absorbance of the solution was recorded using spectro-colorimeter.

The work incorporated in this part of thesis deals with the study of binary complexes of Cu(II), Ni(II), Co(II) and Fe(III) with **Benzoic Acid**, **2-Chlorobenzoic Acid** and **4-Hydroxybenzoic Acid** as a ligands.

1. Metal - Benzoic Acid
2. Metal - 2-Chlorobenzoic Acid
3. Metal - 4-Hydroxybenzoic Acid

Where metal ions are Fe(III)/Cu(II)/Ni(II)/Co(II)

SECTION-II (A)
BENZOIC ACID



LITERATURE SURVEY OF BENZOIC ACID COMPLEXES

Benzoic Acid form stable complexes with a number of metal ions and their stabilities have been determined by different techniques. (5,9).

The ionization constant of benzoic acid has been investigated by B.Saxton and H.F. Meier (12) using conductance measurement at 25°C. Complexes of anthranilic acid and its derivatives with Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) were studied by A. Young and T.R. Sweet (14). Yasuda et-al (13) studied the complexes of benzoic acid and 2-methoxybenzoic acid with Pb(II), Cu(II), Cd(II), Zn(II) and Ni(II) in aqueous solution.

Potentiometric studies of the interaction between Cu(II) and various bidentate chelating agent such as salicylic acid have been made by Heureux and Martell (4). Ramammorthy, Balakrishnan and Santappa (11) also studied complexes of Uranyl ion with mixed carboxylic acids by pH titration method. The above work reveals that Uranyl ion formed only 1:1 complexes with carboxylic acids. W.R. May and M.M. Jones (7) has determined the stability constants of several Copper (II) complexes with seventeen substituted aromatic carboxylic acids, their correlation with the Hammett relationship by the method of Calvin and Wilson and the correction to it was suggested by Van Viter and Hass. The titrations were carried out using a Backman model G.S. pH meter and experimental evidences suggest the formation of 1:1 complex.

P.D. Balton et-al (1) have redetermined the enthalpies and entropies of ionization of benzoic acid and 11-meta and para-substituted benzoic acid. For ten of these compounds emf-Spectrophotometric technique, which has been shown to give reliable results for the heats and entropies of proton ionization (phenol's and anilinium ions) and for which good agreement has been observed between the results obtained and calorimetrically determined.

L.D. Pethe et al (8) have determined the stabilities of $\text{UO}_2(\text{II})$, $\text{Be}(\text{II})$ and $\text{Cu}(\text{II})$ complexes with methoxy substituted benzoic acid in 7.6% (V/V) dioxane in aqueous medium and 0.1M NaClO_4 ionic strength at $30 \pm 0.1^\circ\text{C}$.

Dissociation constants (pK_a) of o-vanilline and stability constants of certain bivalent metal ion complexes have been determined potentiometrically in 50% (V/V) dioxane solution $\mu=0.1$ sodium perchlorate by R.P. Singh et-al (3). Values of the stability constants of these bivalent metal chelates are suggesting there by, that the introduction of methoxy group in salicylaldehyde (i.e. o-vanilline) has no significant effect in the stability of the complexes.

V.K. Mishra and R.K.P. Singh (6) have been determined the stability constants of 4-methoxy benzoate complexes of $\text{Hg}(\text{II})$, $\text{Be}(\text{II})$, $\text{UO}_2(\text{II})$ and $\text{Cu}(\text{II})$ by paper electrophoresis.

Pragya (10) studied binary complexes of $\text{Fe}(\text{III})$, $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Co}(\text{II})$ using 4-aminobenzoic acid and 3-nitrobenzoic acid as primary ligand by Ionophoretic technique at $\mu = 0.1\text{M}$ and 25°C . The stability constant of the complexes were also determined.

The present chapter includes the study of $\text{Fe}(\text{III})$, $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Co}(\text{II})$ Benzoic Acid complexes and observation are recorded in table 2.11, 2.12, 2.13, 2.14 and graphically represented in figures 4.11, 4.12, 4.13, 4.14 in chapter IV.

Table-2.11

Fe (III)- Benzoic Acid		
Fe(III)	= $1 \times 10^{-4}\text{M}$	
Benzoic Acid	= $1 \times 10^{-3}\text{M}$	Blank (A_0)= 0.348
pH	Absorbance (A)	Absorbance Difference (A_0-A)
1.00	0.256	0.092
1.20	0.256	0.092
1.40	0.257	0.091
1.60	0.256	0.092
1.80	0.256	0.092
2.00	0.256	0.092
2.20	0.258	0.090
2.40	0.262	0.086
2.60	0.273	0.075
2.80	0.278	0.070
3.00	0.284	0.064
3.20	0.290	0.058
3.40	0.295	0.053
3.60	0.300	0.048
3.80	0.306	0.042
4.00	0.312	0.036
4.20	0.316	0.032
4.50	0.318	0.030
5.00	0.324	0.024
5.50	0.328	0.020
6.00	0.328	0.020
6.50	0.327	0.021
7.00	0.328	0.020
7.50	0.327	0.021
8.00	0.328	0.020
8.50	0.328	0.020
9.00	0.328	0.020

Table-2.12

Cu (II)- Benzoic Acid		
Cu(II)	$= 1 \times 10^{-3}\text{M}$	
Benzoic Acid	$= 1 \times 10^{-2}\text{M}$	Blank (A_0)= 0.288
pH	Absorbance (A)	Absorbance Difference (A_0-A)
1.00	0.201	0.087
1.20	0.201	0.087
1.40	0.202	0.086
1.60	0.201	0.087
1.80	0.201	0.087
2.00	0.201	0.087
2.20	0.201	0.087
2.40	0.204	0.084
2.60	0.210	0.078
2.80	0.214	0.074
3.00	0.220	0.068
3.20	0.224	0.064
3.40	0.229	0.059
3.60	0.233	0.055
3.80	0.238	0.050
4.00	0.243	0.045
4.20	0.245	0.043
4.50	0.247	0.041
5.00	0.252	0.036
5.50	0.257	0.031
6.00	0.261	0.027
6.50	0.266	0.022
7.00	0.269	0.019
7.50	0.270	0.018
8.00	0.269	0.019
8.50	0.269	0.019
9.00	0.269	0.019

Table-2.13

Ni(II)- Benzoic Acid		
Ni(II)	$= 1 \times 10^{-3}M$	
Benzoic Acid	$= 1 \times 10^{-2}M$	Blank (A_0)= 0.445
pH	Absorbance (A)	Absorbance Difference (A_0-A)
1.00	0.296	0.149
1.20	0.296	0.149
1.40	0.297	0.148
1.60	0.296	0.149
1.80	0.296	0.149
2.00	0.297	0.148
2.20	0.296	0.149
2.40	0.296	0.149
2.60	0.307	0.138
2.80	0.317	0.128
3.00	0.327	0.118
3.20	0.338	0.107
3.40	0.349	0.096
3.60	0.359	0.086
3.80	0.369	0.076
4.00	0.380	0.065
4.20	0.385	0.060
4.50	0.391	0.054
5.00	0.401	0.044
5.50	0.410	0.035
6.00	0.421	0.024
6.50	0.430	0.015
7.00	0.434	0.011
7.50	0.434	0.011
8.00	0.434	0.011
8.50	0.434	0.011
9.00	0.434	0.011

Table-2.14

Co(II)- Benzoic Acid		
Co(II)	$= 1 \times 10^{-3}\text{M}$	
Benzoic Acid	$= 1 \times 10^{-2}\text{M}$	Blank (A_0)= 0.365
pH	Absorbance (A)	Absorbance Difference (A_0-A)
1.00	0.213	0.152
1.20	0.213	0.152
1.40	0.212	0.153
1.60	0.213	0.152
1.80	0.212	0.153
2.00	0.213	0.152
2.20	0.213	0.152
2.40	0.213	0.152
2.60	0.213	0.152
2.80	0.227	0.138
3.00	0.240	0.125
3.20	0.254	0.111
3.40	0.265	0.100
3.60	0.282	0.083
3.80	0.299	0.066
4.00	0.310	0.055
4.20	0.315	0.050
4.50	0.323	0.042
5.00	0.337	0.028
5.50	0.352	0.013
6.00	0.357	0.008
6.50	0.356	0.009
7.00	0.357	0.008
7.50	0.358	0.007
8.00	0.357	0.008
8.50	0.357	0.008
9.00	0.357	0.008

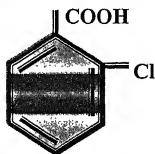
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SECTION -II (B)

2-CHLOROBENZOIC ACID



LITERATURE SURVEY OF 2-CHLOROBENZOIC ACID COMPLEXES

2-Chlorobenzoic Acid have been used as a ligand in a number of complexes and their stabilities have been determined by different methods (11,14).

The stability constants various metal complexes of 2-chloro, 3-chloro, 2-bromo benzoic acids were evaluated by Dippy, Williams and Lewis (4). In 1936, Dippy and Lewis (5) also evaluated the stability constants of complexes of 3-bromobenzoic acid. Everett, and Wynne Jones (6) have also worked with 2-chlorobenzoic acid.

Using potentiometric titration method the interaction of Uranyl ions with 3-bromo, 3,5 dichloro, 5-chloro and 4-iodo salicylic acids have been investigated by Jahagirdar and Khanolkar (8). Wilson, Gore, Sawbridge and Cardenas-Guz (18) studied the stability constants of 3-chlorobenzoic acid, 4-chlorobenzoic acid, 3-bromobenzoic acid and 4-bromobenzoic acid, while Briegleb and Bieber (2) worked with 3-chlorobenzoic acid and 4-bromobenzoic acid.

Mahadevan et-al (9) have determined the stability of the complex of catechol and picolinic acid with some metal ions by using potentiometric method. The studies, however indicate that it is not possible to include $\text{UO}_2(\text{II})$, $\text{Be}(\text{II})$ and $\text{Cu}(\text{II})$ in any general stability order. Mahadevan et-al (10) have suggested that the stability order enunciated by Irving and Williams (7) has been extended by Bosalo and Pearson to include many other divalent ions. Their order of stability is :



May and Jones (12) have determined the stability constants of several Copper (II) complexes with seventeen substituted aromatic carboxylic acids, their correlation with the Hammett relationship by the method of Calvin and Wilson and the correction to it was suggested by

Van Vitert and Hass. The titrations were carried out using a Backman model GS pH meter and experimental evidences suggest the formation of 1:1 complex.

Heat of ionization of several organic acids were evaluated by calorimetric method by Cottrell, Drake, Levi, Tully and Wolfeded (3). Balton, Flemming and Hall (1) studied free energy, enthalpy, entropy relationship for ionization of p-chlorobenzoic acid and p-bromobenzoic acid. The ionization constant of three mono chlorobenzoic acids were investigated by Saxton and Meier (17).

Rai (16) have determined the stability constant of 2-chlorobenzoate complexes of $\text{UO}_2(\text{II})$, $\text{Cu}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Pb}(\text{II})$ and $\text{Th}(\text{IV})$ by paper electrophoresis technique. Nathaniel A.K. (13) studied the stability constant of o-bromo, m-bromo, and p-bromo benzoate complexes of $\text{UO}_2(\text{II})$, $\text{Pb}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Mn}(\text{II})$ by paper electrophoresis.

Pragya (15) studied the binary complexes of $\text{Fe}(\text{III})$, $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Co}(\text{II})$ with 2-bromobenzoic acid and determined the stability constant of the benzoate complexes by Ionophoretic technique at $\mu = 0.1\text{M}$ and 25°C .

The present chapter includes the study of $\text{Fe}(\text{III})$, $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Co}(\text{II})$ -2-Chlorobenzoic Acid complexes and observation are recorded in tables 2.15, 2.16, 2.17, 2.18 and graphically represented in figures 4.15, 4.16, 4.17, 4.18 in chapter IV.

Table-2.15

Fe (III) - 2-Chlorobenzoic Acid		
Fe(III)	$= 1 \times 10^{-4}M$	
2-Chlorobenzoic Acid	$= 1 \times 10^{-3}M$	
	Blank (A_0) = 0.348	
pH	Absorbance (A)	Absorbance Difference ($A_0 - A$)
1.00	0.256	0.092
1.20	0.256	0.092
1.40	0.257	0.091
1.60	0.256	0.092
1.80	0.263	0.085
2.00	0.273	0.075
2.20	0.289	0.059
2.40	0.298	0.050
2.60	0.306	0.042
2.80	0.313	0.035
3.00	0.317	0.031
3.20	0.319	0.029
3.40	0.320	0.029
3.60	0.321	0.027
3.80	0.320	0.028
4.00	0.320	0.028
4.20	0.320	0.028
4.50	0.320	0.028
5.00	0.319	0.028
5.50	0.320	0.028
6.00	0.321	0.027
6.50	0.320	0.028
7.00	0.319	0.026
7.50	0.320	0.028
8.00	0.320	0.028
8.50	0.320	0.028
9.00	0.320	0.028

Table-2.16

Cu (II) - 2-Chlorobenzoic Acid		
= $1 \times 10^{-3}M$		
2-Chlorobenzoic Acid = $1 \times 10^{-2}M$		Blank (A_0)= 0.288
pH	Absorbance (A)	Absorbance Difference (A_0-A)
1.00	0.201	0.087
1.20	0.201	0.087
1.40	0.201	0.087
1.60	0.201	0.087
1.80	0.201	0.087
2.00	0.213	0.075
2.20	0.226	0.062
2.40	0.238	0.050
2.60	0.250	0.038
2.80	0.261	0.027
3.00	0.261	0.027
3.20	0.262	0.026
3.40	0.261	0.027
3.60	0.260	0.028
3.80	0.261	0.027
4.00	0.261	0.027
4.20	0.261	0.027
4.50	0.261	0.027
5.00	0.261	0.027
5.50	0.262	0.026
6.00	0.261	0.027
6.50	0.262	0.026
7.00	0.261	0.027
7.50	0.261	0.027
8.00	0.261	0.027
8.50	0.261	0.027
9.00	0.261	0.027

Table-2.17

Ni (II) - 2-Chlorobenzoic Acid Ni(II) $= 1 \times 10^{-3}M$ 2-Chlorobenzoic Acid $= 1 \times 10^{-2}M$ Blank (A_0) = 0.445		
pH	Absorbance (A)	Absorbance Difference ($A_0 - A$)
1.00	0.296	0.149
1.20	0.296	0.149
1.40	0.296	0.149
1.60	0.296	0.149
1.80	0.296	0.149
2.00	0.296	0.149
2.20	0.317	0.128
2.40	0.347	0.098
2.60	0.387	0.058
2.80	0.417	0.028
3.00	0.428	0.017
3.20	0.429	0.016
3.40	0.428	0.017
3.60	0.428	0.017
3.80	0.428	0.017
4.00	0.428	0.017
4.20	0.429	0.016
4.50	0.428	0.017
5.00	0.428	0.017
5.50	0.429	0.016
6.00	0.428	0.017
6.50	0.427	0.018
7.00	0.428	0.017
7.50	0.428	0.017
8.00	0.428	0.017
8.50	0.428	0.017
9.00	0.428	0.017

Table-2.18

Co(II) - 2-Chlorobenzoic Acid		
Co(II)	$= 1 \times 10^{-3}M$	
2-Chlorobenzoic Acid	$= 1 \times 10^{-2}M$	
	Blank (A_0) = 0.365	
pH	Absorbance (A)	Absorbance Difference ($A_0 - A$)
1.00	0.213	0.152
1.20	0.212	0.153
1.40	0.213	0.152
1.60	0.212	0.153
1.80	0.213	0.152
2.00	0.213	0.152
2.20	0.213	0.152
2.40	0.240	0.125
2.60	0.317	0.048
2.80	0.349	0.016
3.00	0.350	0.015
3.20	0.349	0.016
3.40	0.349	0.016
3.60	0.348	0.017
3.80	0.349	0.016
4.00	0.349	0.016
4.20	0.349	0.016
4.50	0.349	0.016
5.00	0.347	0.018
5.50	0.349	0.016
6.00	0.349	0.016
6.50	0.348	0.017
7.00	0.349	0.016
7.50	0.349	0.016
8.00	0.349	0.016
8.50	0.349	0.016
9.00	0.349	0.016

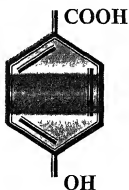
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Sawbridge, J.E.; and
Cardenas-Guz. F.;

SECTION -II (C)

4-HYDROXYBENZOIC ACID



LITERATURE SURVEY OF 4-HYDROXYBENZOIC ACID COMPLEXES

As a matter of fact 4-Hydroxybenzoic Acid has two donor oxygen atom. It forms a number of stable complexes with different metal ions. A variety of these 4-hydroxybenzoic acid complexes have been investigated by several workers using different techniques. The stability constants of the so formed complexes have been compiled by Martell (10) and Perrin (15).

Babko (2) studied the nature of the Aluminium(III)-salicylate complex by the displacement method. A colour was developed by mixing Ferric (III) and salicylic acid and the decrease in intensity was measured on addition of Aluminium(III) solution. Assuming the complex to be similar to that of Iron complex, he calculated the complexation constant. He also measured the ultraviolet, absorption spectra of solution of salicylic acid and salicylic acid mixed with aluminium nitrate and calculated the stability constant of the complex. Meeks and Bank (11) with the help of spectrophotometric method studied the Beryllium(II)-salicylate and Beryllium (II)-sulphosalicylate complexes.

Fe(III)-salicylic acid complexes have been extensively studied by Chanley et-al (4) in 50% methanol. Maintaining pH between 1.5 and 2 ($\mu=0.2$, 25°C) they have determined the ionization constants of the acid and stability constant of the various ion complexes formed.

The dissociation constants of nine substituted salicylic acids have been determined together with those of 3-hydroxy-2-naphthoic acid and it's methyl ether by Bray et-al (3). The dissociation constants of salicylic acid and it's meta and para isomers have also been measured for the first time by a modern conductometric procedure. The evidence suggests that in the 6-substituted salicylic acids the measured strength is an out come of completing ortho-effects.

Using spectrophotometric method Verma & Mehrotra (20) studied the Beryllium(II)-salicylate and Beryllium (II)-sulphosalicylate complexes. Das and Aditya (6) have used the spectrophotometric technique in the study of Aluminium-salicylic acid complex from, which they have determined the composition of the complex by job's method of continued variation. Stability constant of the complex has been calculated from the optical density measurements. Das and Aditya also studied the complex formation of Beryllium with salicylic and sulphosalicylic acid by ultraviolet spectroscopy (7). They observed that Beryllium perchlorate (Be^{+2}), forms colourless complex with salicylic as well as with sulphosalicylic acid. The absorption spectra at different pH's suggest that the complex formation increases with an increase in pH. Following Job's method of continued variation at pH 4.5, the composition of these complexes have been studied. The molecular ratio of Beryllium (II) to the ligand in both the complexes is 1:1. At ionic strengths of 0.02, 0.05, 0.1 and 0.2 the stability constants were determined. The value of $-\Delta F$ for Beryllium(II)-salicylate were found to be 5830 and 6010 calories respectively.

Potentiometric studies of the interaction between Cu(II) and various bidentate, chelating, salicylic acids have been made by Heureux and Martell (8). Study of mixed ligand complexes of Cu(II) containing salicylic acid also as liganding species have been made by Perrin and Co-workers (14). Condike and Martell (5) also studied the mixed ligand chelates of copper (II) in which salicylic acid was also a ligand.

The interaction of Uranyl ion with salicylic acid and 4-hydroxy and 5-hydroxy salicylic acids have been investigated by potentiometric titration by Jahagirdar and Khanolkar (9). The stability constants of complexes containing 1:1 and 1:2 ratio's of Uranyl(II)-ligand have been estimated at 31°C and 0.1M NaClO_4 ionic strength in aqueous medium. A dichelates of Ti(III) with salicylic acid and sulphosalicylic acids Viz. $[\text{Ti}(\text{C}_7\text{H}_5\text{O}_3)_2\text{OH}.\text{OH}_2]3\text{H}_2\text{O}$ and $[\text{Ti}(\text{C}_7\text{H}_5\text{SO}_6)_2\text{OH}.\text{OH}_2]3\text{H}_2\text{O}$ and the

trichelates, Viz. $[\text{Ti}(\text{C}_7\text{H}_5\text{O}_3)_3]_2\text{H}_2\text{O}$ and $[\text{Ti}(\text{C}_7\text{H}_5\text{SO}_6)_3]$ respectively have been prepared by Aggarwal and Shrivastava (1). Infrared spectral data confirms the structure proposed for di and tri-chelates. Potentiometric measurements for the Tellurium(III)-salicylate and Tellurium(III)-sulphosalicylate complexes indicated the formation of a 1:1 complex. Panchal and Bhattacharya(12) using Irving Rossotti method studied the Beryllium(II) Zinc(II) and Vanadyl(II)-salicylate and thiosalicylate complexes. The relative values of the formation constants have been interpreted in term of class A and class B character of the metal ions and also on the basis of M-S π interaction.

The stability constants of Zn(II), Co(II), Uranyl(II) and Chromium (IV) salicylate complexes have been determined by Singh and Coworkers (17) at an ionic strength 0.1M and 40°C. They also (18) studied the stability constants of salicylate complexes of Cu(II) and Ni(II) by paper electrophoresis at 40°C and an ionic strength 0.1M.

Suk et-al (19) studied the thermodynamic parameters of formation of 1:1 complexes between lanthanide cations and some benzoic acid derivatives by potentiometric and calorimetric methods in aqueous solution at $\mu=0.1\text{M}$ and 25°C. Patel and Singh (13) studied the stability constant of salicylate complex of Fe(III), Cu(II), Ni(II) and Co(II) by Ionophoretic technique at $\mu = 0.1\text{M}$ and 25°C.

The present chapter includes the study of Fe(III), Cu(II), Ni(II) and Co(II)-4-Hydroxybenzoate complexes and the observations are recorded in tables 2.19, 2.20, 2.21, 2.22 and graphically represented in figure 4.19, 4.20, 4.21, 4.22 in chapter IV.

Table-2.19

Fe (III) - 4-Hydroxybenzoic Acid		
Fe(III)	$= 1 \times 10^{-4}\text{M}$	
4-Hydroxybenzoic Acid	$= 1 \times 10^{-3}\text{M}$	
	Blank (A_0) = 0.348	
pH	Absorbance (A)	Absorbance Difference ($A_0 - A$)
1.00	0.256	0.092
1.40	0.257	0.091
1.80	0.256	0.092
2.00	0.256	0.092
2.40	0.256	0.092
2.80	0.257	0.091
3.00	0.261	0.087
3.20	0.265	0.083
3.40	0.270	0.078
3.60	0.275	0.073
3.80	0.281	0.067
4.00	0.291	0.057
4.20	0.297	0.051
4.40	0.302	0.046
4.60	0.306	0.042
4.80	0.310	0.038
5.00	0.315	0.033
5.20	0.319	0.029
5.40	0.323	0.025
5.60	0.324	0.024
6.00	0.324	0.024
6.50	0.324	0.024
7.00	0.324	0.024
7.50	0.325	0.023
8.00	0.324	0.024
8.50	0.324	0.024
9.00	0.324	0.024

Table-2.20

Cu(II) - 4-Hydroxybenzoic Acid		
Cu(II)	$= 1 \times 10^{-3}\text{M}$	
4-Hydroxybenzoic Acid	$= 1 \times 10^{-2}\text{M}$	Blank (A_0) = 0.288
pH	Absorbance (A)	Absorbance Difference ($A_0 - A$)
1.00	0.201	0.087
1.40	0.201	0.087
1.80	0.202	0.086
2.00	0.201	0.087
2.40	0.201	0.087
2.80	0.201	0.087
3.00	0.201	0.087
3.20	0.210	0.078
3.40	0.214	0.074
3.60	0.218	0.070
3.80	0.222	0.066
4.00	0.227	0.061
4.20	0.231	0.057
4.40	0.235	0.053
4.60	0.240	0.048
4.80	0.244	0.044
5.00	0.248	0.040
5.20	0.252	0.036
5.40	0.261	0.027
5.60	0.265	0.023
6.00	0.266	0.022
6.50	0.265	0.023
7.00	0.266	0.023
7.50	0.266	0.022
8.00	0.265	0.023
8.50	0.265	0.023
9.00	0.265	0.023

Table-2.21

Ni(II) - 4-Hydroxybenzoic Acid Ni(II) = $1 \times 10^{-3}M$ 4-Hydroxybenzoic Acid = $1 \times 10^{-2}M$		
		Blank (A_0) = 0.445
pH	Absorbance (A)	Absorbance Difference ($A_0 - A$)
1.00	0.296	0.149
1.40	0.295	0.150
1.80	0.296	0.149
2.00	0.296	0.149
2.40	0.296	0.149
2.80	0.296	0.149
3.00	0.306	0.139
3.20	0.316	0.129
3.40	0.326	0.119
3.60	0.336	0.109
3.80	0.345	0.100
4.00	0.356	0.089
4.20	0.368	0.077
4.40	0.376	0.069
4.60	0.385	0.060
4.80	0.395	0.050
5.00	0.405	0.040
5.20	0.415	0.030
5.40	0.425	0.020
5.60	0.432	0.013
6.00	0.431	0.014
6.50	0.432	0.013
7.00	0.433	0.012
7.50	0.432	0.013
8.00	0.432	0.013
8.50	0.432	0.013
9.00	0.432	0.013

Table-2.22

Co(II) - 4-Hydroxybenzoic Acid		
Co(II)	$= 1 \times 10^{-3}M$	
4-Hydroxybenzoic Acid	$= 1 \times 10^{-2}M$	
	Blank (A_0) = 0.365	
pH	Absorbance (A)	Absorbance Difference ($A_0 - A$)
1.00	0.213	0.152
1.40	0.213	0.152
1.80	0.212	0.153
2.00	0.213	0.152
2.40	0.212	0.153
2.80	0.213	0.152
3.00	0.213	0.152
3.20	0.213	0.152
3.40	0.225	0.140
3.60	0.235	0.130
3.80	0.247	0.118
4.00	0.259	0.106
4.20	0.270	0.095
4.40	0.280	0.085
4.60	0.293	0.072
4.80	0.305	0.060
5.00	0.317	0.048
5.20	0.326	0.039
5.40	0.340	0.025
5.60	0.353	0.012
6.00	0.353	0.012
6.50	0.352	0.013
7.00	0.353	0.012
7.50	0.352	0.013
8.00	0.353	0.012
8.50	0.353	0.012
9.00	0.353	0.012

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CHAPTER - III

STUDY OF TERNARY COMPLEXES

STUDY OF TERNARY COMPLEXES

A BRIEF REVIEW OF METAL COMPLEXES

Nitrilotriacetic acid (NTA) is an excellent polydentate ligand and form very stable complexes with a large number of metal ions at lower pH (68, 18, 8, 14, 42). It behave as a tridentate (70) or tetradentate (23) ligand depending upon the nature of the metal ions. The metal NTA complexes are formed at lower pH and do not undergo dissociation or hydroxo complex formation at higher pH (9). In the case of M-NTA complexes, where metal ions have coordination number more than four, the vacant positions are occupied by water molecule at low pH.

Puschell & Lassener (36) indicated the existence of a ternary complex by sorption studies upon dowex chelating resin A-1 and the weakening of the colour of the niobium-methyl thymol hydrogen peroxide complex (27) which leads to the colorimetric estimation of the metal. The mixed complexes are often found to be more stable than the binary complexes (48) which is attributed to :

- (1) Statistical effect (30, 7)
- (2) Formation of bonds between the ligands of different type (69)
- (3) Increased polarization of the metal ion (31, 58)
- (4) Charge neutralization with decreased solvation (43)
- (5) Assymetry of the ligand field (15, 5)

Tandon et-al (63, 64) observed effective removal of Manganese from rats liver with the help of NTA. Longman and Coworkers (28) re-examined its significance in chemistry. Nitrilotriacetic acid has been used as chelating agent in the metal intoxication. Jorgenson and Nolan (24, 35) and Sharp (47) have investigated the effect on cadmium toxicity in rats. Tabatabai et-al (62) determined the amounts of NTA in soils using photometric technique and developed the method for removing the effect

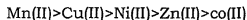
of metal interferences using a chelating resin. Effect of NTA on blood coagulation and on growth and mating of *E. coli* has been studied by Stin (60). NTA present in trace amounts in tap water was determined by Robinson and Lott (38), on the basis of quenching of the fluorescence of the gallium-8-quinolinol complex by NTA (Nitrilotriacetic acid).

The absorption spectra of the ternary Molybdenum/ Vanadium-NTA-hydrogen peroxide complex has been studied by Cheng and Lott (10). The Fe(III)-NTA-Catechol-3,5-disulphonic acid was investigated by Schwarzenbach and Willi (44). Metal - NTA amino acid systems have been extensively studied by Israeli et-al (20, 21). The coordination of ethyl valinate with M-NTA negative complexes shows a trend significantly different from that of glycine. Jiril Stray (61) using solvent extraction method reported ML and ML₂ complexes of bivalent metal ions.

Thermodynamic study of reaction between various bivalent cation and nitrilotriacetic acid as a ligand has been made by Hull and Coworkers (18). They assessed the heat of formation of the 1:1 complexes of Cu(II), Co(II), Mn(II), Ni(II), Zn(II), Ca(II) and Sr(II) with NTA. They also reported the 1:2 complex of Cu(II). Variations in the stability of these complexes was attributed to the differences in the entropies of formation.

Irving and Coworkers (19) observed that substitution of a hydrogen by a methyl group in amino polycarboxylic acid decreased the acid dissociation constants but the stability constant of its metal complexes did not increase proportionally due to steric factor. The liganding property of various derivatives of NTA with bivalent metal ion was enhanced and found the increase in the stability constant at $\mu = 0.1$ (KCl) to be in following order Ba(II) > Sr(II) > Mg(II) > Ca(II) > Zn(II). Studies of the complexes of Aluminum with some polyamino polycarboxylic acids were made potentiometrically by Bhat et al (6). Hopgood and Co-workers (17) investigated the interaction of amino acids and their esters with bivalent metal nitrilotriacetate complexes. It was found that the formation constant

of mixed complexes of the type M-NTA-glycine follow the Irving Williams order.



Spectrophotometric study of the system Zn-NTA-Eriochrome black T, has been made by Kodama and Ebine (26). Yoshimura and Tamura (71) spectrophotometrically studied the Chromium(VI)-NTA complex in dimethyl formamide as the solvent and Martinez et-al (29) worked out a photometric determination of the metal. Ramamoorthy et-al (37) and Dey et-al (3) have examined the complexes of Fe(III) and Cu (II) with NTA as a primary ligand and a series of oxygen bonding organic anions as secondary ligands. Jakob and Margerum (22) evaluated the formation constant of the system Ni(II)-NTA oxalic acid.

Ternary system of the type M-NTA-L where M = Cu, Ni, L= ligand viz: thiourea, phenyl thiourea were studied by chidambaram and Bhattacharya (11). Mixed complexes of glycine, valine along with M-NTA were studied by Srivastava et-al (59) electrometrically. Dwivedi & Dey (13) studied the ternary complexes of Cu(II) and Zn (II) by employing o-cresotic acid, m-cresotic acid and 2-hydroxy-3-naphthoic acid as secondary ligands and NTA as a primary ligands. Bagchi and Dey (4) investigated the complexes of Cu(II) with adenine, hydroxanthine, xanthine and guanosine as secondary ligands. The ternary complexes of Cu(II), Zn(II), Ni(II), Co(II) and Cd(II) with azoquinine or taurine as secondary ligands were studied by Mittal and Dey (34).

Yadava and Coworkers (51,52) investigated ternary complexes of the type M(II)-glutaric acid-NTA and M-adipic acid-NTA by paper electrophoresis. They have also studied the M(II)-NTA-asparatic acid complexes (56) by applying the same technique.

Potentiometric studies of ternary Cu(II)-complexes of some purine derivatives using, NTA as a primary ligand has been done by Ghosh and Dey (16) at 25°C and $\mu = 0.1\text{M}$ (KNO_3). They also studied

binary complexes and compared the formation constants of the ternary complexes with that of binary complexes.

Joshi (25) has applied the Irving Rosotti titration technique for the study of mixed ligand formation constant of the type MAL where $M = \text{Zn}$ and Cd , $A = \text{NTA}$ and $L = \text{amino acids}$. The value of mixed ligand formation constant K_{MAL}^{M-L} are lower than $K_{\text{ML}_2}^{\text{ML}}$. Singh et-al (53) employed the ionophoretic technique in the study of mixed complexes (M-NTA-Valinate systems). They calculated the stability constants of complexes M-NTA-Valinate which are found to be 5.25, 5.18, 3.25, 3.17 (log K values) for Cu(II), UO₂(II), Co(II) and Zn(II) respectively at ionic strength 0.1M (NaClO₄) and 35°C.

A new ionophoretic technique for the study of metal complexes in solution has been used by Singh et-al (54). The complexes of Cu(II) and Fe(III) with glycine has been studied and the stability constants of the various complexes formed have been determined at 25°C and $\mu = 0.1\text{M}$ (NaClO₄). For the experimental studies, a simple electrophoretic tube has been designed which yields good results after standardization. Cu(II) and Al(III) glutamate complexes have also been studied by Singh et al using the same technique. Singh et-al (55) have studied the ternary complexes of Cu(II), Zn(II) and Cd(II) with NTA as primary ligand and glutamic acid as secondary ligand at 35°C and $\mu = 0.1\text{M}$ (NaClO₄) by using ionophoretic technique.

Mishra V. K. et-al (32) determined the stability constant of Be(II), UO₂(II), Hg(II) and Cu(II) complexes with NTA and 3-hydroxybenzoic acid by electrophoretic method at 35°C & $\mu = 0.1\text{M}$ (NaClO₄). Sarkar (41) studied electrophoretically the ternary complexes of Cu(II), Ni(II), Co(II), UO₂(II) with citrate and nitrilotriacetate in solution. The electrophoretic studies of ternary complexes with metal ions Hg (II), Be(II), and Cu(II) has been done by Mishra et-al (33), where NTA as primary and adenine as secondary ligand were used.

Das and Srivastava (12) studied the mixed ligand complexes of Cu(II), Ni(II), Co(II) and Zn(II) with NTA and aminodiacetic acid as primary ligand by potentiometric method in 50% aqueous medium which follow the order Cu(II), Co(II), Zn(II), Ni(II). The mixed ligand complexes of Hg(II), Be(II), Ni(II) with methyl cysteine (sulphur containing amino acid) as a primary ligand and penicillamine as secondary ligand were studied by Tiwari et-al (65) by using paper electrophoresis and the stability constants were also determined. They also studied the binary complexes of M-methyl cysteine system and compared the binary system with that of the ternary system by using penicillamine as a secondary ligand.

Ternary complexes of Cu(II), Ni(II) and Co(II) with malonic acid/succinic acid/ glutaric acid/ adipic acid as primary ligands and NTA as secondary ligand have been studied by Shagufta Zamani (45) with the help of ionophoretic technique at $\mu = 0.1\text{M}$ and 30°C . She has also studied the binary complexes of the above mentioned metal ions and ligands. Using the same ionophoretic technique M.P. Singh (57) has studied the ternary complexes Cu(II), Zn(II), Fe(III) with alanine and phenyl alanine as primary ligand and NTA as secondary ligand.

Amita and Coworkers (2) investigated the mixed ligand complexes of Co(II) and Cu(II) with adenosine diphosphate as a primary ligand and NTA as a secondary ligand by an ionophoretic technique (Paper electrophoresis) and they also calculated the stability constant values. The mixed ligand complexes of Zn^{+2} and Cd^{+2} with methyl cysteine and cysteine were studied by Tiwari et-al (66) by an electrophoretic method. Using the same technique he also studied the mixed ligand complexes of Hg^{+2} , Be^{+2} and Ni^{+2} with methyl cysteine as a primary ligand and cysteine as a secondary ligand, and the stability constants of the complexes formed were determined (67).

The ternary metal complexes of Fe(III), Cu(II), Ni(II) and Co(II) by using asparagine, glutamine and aspartic acid as a primary ligand and

nitrilotriacetic acid as a secondary ligand have been studied by Sharmila (46) by ionophoresis at an ionic strength 0.1M and 30°C. The stability constants of these complexes have also been calculated.

Anand Swaroop (1) studied the ternary complexes of Cu(II), Ni(II) and Zn(II) with AMP, ADP and ATP as a primary ligand and nitrilotriacetic acid as a secondary ligand at 30°C and 0.1M by using ionophoretic technique.

Sameena (39) investigated the ternary complexes of Ni(II) and Co(II) with serine as a primary ligand and nitrilotriacetic acid as a secondary ligand at 25°C and 0.1M NaClO₄ by using ionophoretic technique. The ternary complexes of Ni(II) and Co(II) using leucine as a primary ligand and NTA as a secondary ligand and the ternary complexes of Fe (III), Cu (II), Ni (II) and Co(II) using serine as a primary ligand and leucine as secondary ligand have also been studied by her (40).

R.K.P. Singh and R.P. Patel (49) investigated the ternary complexes of Fe(III), Cu(II), Ni(II) and Co(II) with salicylate as a primary ligand and nitrilotriacetic acid as a secondary ligand at 25°C and 0.1M NaClO₄ by using ionophoretic technique. They have (50) also investigated the ternary metal complexes of Fe(III) and Zn(II) with adipate as a primary ligand and nitrilotriacetic acid as a secondary ligand.

The work incorporated in this part of thesis deals with the study of mixed metal ligands complexes of Cu(II), Ni(II), Co(II) and Fe(III) with **Benzoic Acid**, **2-Chlorobenzoic Acid** and **4-Hydroxybenzoic Acid** as primary ligands and **NTA** as a secondary ligand.

This ternary system studies include :

1. Fe (III)-Benzoic Acid/2-Chlorobenzoic Acid/4-Hydroxybenzoic Acid-NTA
2. Cu (II)-Benzoic Acid/2-Chlorobenzoic Acid/4-Hydroxybenzoic Acid-NTA
3. Ni (II)-Benzoic Acid/2-Chlorobenzoic Acid/4-Hydroxybenzoic Acid- NTA
4. Co (II)-Benzoic Acid/2-Chlorobenzoic Acid/4-Hydroxybenzoic Acid-NTA

EXPERIMENTAL

NTA SOLUTION :

Nitrilotriacetic acid of G.R. grade was used.

A 10^{-3} M solution of NTA was prepared by weight, in double distilled water. For the present study of mixed complexes, NTA concentration range from 10^{-6} M to 10^{-2} M strength. The strength of NTA for binary complexes was kept at 0.2×10^{-2} M for Cu(II), Ni(II), Co(II) and 0.2×10^{-3} M for Fe(III).

METAL IONS :

The 1×10^{-3} M solution of Cu(II), Ni(II), Co(II) and 1×10^{-4} M solution of Fe(III) were prepared as described earlier.

BACKGROUND ELECTROLYTE :

The background electrolyte consists of 0.1M perchloric acid. This was prepared as described earlier.

PROCEDURE

For the investigation of mixed ligand complexes of metal ions with benzoic acid, 2-chlorobenzoic acid and 4-hydroxybenzoic acid as a primary ligand and NTA as a secondary ligand the experimental procedure was modified. An appropriate reaction mixture containing metal ions and $1 \times 10^{-2} \text{M}$ benzoic acid/2-chlorobenzoic acid/4-hydroxybenzoic Acid and 0.1M perchloric acid is adjusted to pH 7 by adding caustic soda. The reason behind keeping the reaction mixture at pH 7 is that much ahead of this pH, the simple binary complexes of metal ions with primary ligands are formed and remain intact even beyond this pH.

To this solution the conc. of secondary ligand (NTA) was increased gradually and the electrophoretic observations were made at every addition of NTA. The NTA concentration range was kept initially at 10^{-6}M and increased gradually upto 10^{-2}M . All the observations were recorded under the following conditions.

10ml of the solution was electrolysed in the electrophoretic tube, under the potential gradient of 50 volts DC for 45 minutes. The contents of the anodic compartment were analysed for metal ions using suitable developing reagents. These observations were repeated at several concentrations of NTA. The observations thus found have been depicted in table (3.11, 3.12, 3.13, 3.14, 3.15, 3.16, 3.17, 3.18, 3.19, 3.20, 3.21, 3.22) in subsequent pages.

SECTION -III (A)
METAL- BENZOIC ACID -NTA SYSTEMS

Table-3.11

Fe (III) - Benzoic Acid-NTA System		
Fe(III)	= $1 \times 10^{-4}\text{M}$	
Benzoic Acid	= $1 \times 10^{-3}\text{M}$	Blank (A_0)= 0.348
-log[NTA]	Absorbance (A)	Absorbance Difference (A_0-A)
6.00	0.328	0.020
5.00	0.329	0.019
4.70	0.328	0.020
4.40	0.328	0.020
4.20	0.328	0.020
4.10	0.328	0.020
4.00	0.328	0.020
3.70	0.333	0.015
3.40	0.356	-0.008
3.20	0.371	-0.023
3.10	0.379	-0.031
3.00	0.387	-0.039
2.70	0.408	-0.060
2.40	0.408	-0.060
2.20	0.409	-0.061
2.10	0.408	-0.060
2.00	0.408	-0.060

Table-3.12

Cu (II) - Benzoic Acid-NTA System		
Cu(II)	= $1 \times 10^{-3}\text{M}$	
Benzoic Acid	= $1 \times 10^{-2}\text{M}$	Blank (A_0) = 0.288
-log[NTA]	Absorbance (A)	Absorbance Difference ($A_0 - A$)
6.00	0.269	0.019
5.00	0.269	0.019
4.70	0.270	0.018
4.40	0.269	0.019
4.20	0.269	0.019
4.10	0.269	0.019
4.00	0.269	0.019
3.70	0.271	0.017
3.40	0.303	-0.015
3.20	0.319	-0.031
3.10	0.329	-0.041
3.00	0.339	-0.051
2.70	0.370	-0.082
2.40	0.371	-0.083
2.20	0.370	-0.082
2.10	0.370	-0.082
2.00	0.370	-0.082

Table-3.13

Ni (II) - Benzoic Acid-NTA System		
Ni(II)	$= 1 \times 10^{-3}\text{M}$	
Benzoic Acid	$= 1 \times 10^{-2}\text{M}$	Blank (A_0) = 0.445
$-\log[\text{NTA}]$	Absorbance (A)	Absorbance Difference ($A_0 - A$)
6.00	0.434	0.011
5.00	0.433	0.012
4.70	0.434	0.011
4.40	0.434	0.011
4.20	0.434	0.011
4.10	0.433	0.012
4.00	0.434	0.011
3.70	0.434	0.011
3.40	0.452	-0.007
3.20	0.487	-0.042
3.10	0.503	-0.058
3.00	0.520	-0.075
2.70	0.556	-0.111
2.40	0.557	-0.112
2.20	0.556	-0.111
2.10	0.556	-0.111
2.00	0.556	-0.111

Table-3.14

Co (II) - Benzoic Acid-NTA System		
Co(II)	$= 1 \times 10^{-3} \text{M}$	
Benzoic Acid	$= 1 \times 10^{-2} \text{M}$	Blank (A_0) = 0.365
$-\log[\text{NTA}]$	Absorbance (A)	Absorbance Difference ($A_0 - A$)
6.00	0.357	0.008
5.00	0.357	0.008
4.70	0.358	0.007
4.40	0.357	0.008
4.20	0.357	0.008
4.10	0.357	0.008
4.00	0.357	0.008
3.70	0.357	0.008
3.40	0.357	0.008
3.20	0.400	-0.035
3.10	0.420	-0.055
3.00	0.440	-0.075
2.70	0.483	-0.118
2.40	0.482	-0.117
2.20	0.483	-0.118
2.10	0.483	-0.118
2.00	0.483	-0.118

SECTION -III (B)

METAL-2-CHLOROBENZOICACID-NTA SYSTEMS

Table-3.15

Fe (III) - 2-Chlorobenzoic Acid-NTA System		
Fe(III)	= $1 \times 10^{-4}\text{M}$	
2-Chlorobenzoic Acid	= $1 \times 10^{-3}\text{M}$	Blank (A_0)= 0.348
-log[NTA]	Absorbance (A)	Absorbance Difference ($A_0 - A$)
6.00	0.320	0.028
5.00	0.320	0.028
4.70	0.320	0.028
4.40	0.331	0.017
4.20	0.343	0.005
4.10	0.348	0.000
4.00	0.358	-0.006
3.70	0.371	-0.023
3.40	0.388	-0.040
3.20	0.400	-0.052
3.10	0.405	-0.057
3.00	0.411	-0.063
2.70	0.416	-0.068
2.40	0.415	-0.067
2.20	0.416	-0.068
2.10	0.416	-0.068
2.00	0.416	-0.068

Table-3.16

Cu (II) - 2-Chlorobenzoic Acid-NTA System		
Cu(II)	= $1 \times 10^{-3}\text{M}$	
2-Chlorobenzoic Acid	= $1 \times 10^{-2}\text{M}$	Blank (A_0)= 0.288
-log[NTA]	Absorbance (A)	Absorbance Difference ($A_0 - A$)
6.00	0.261	0.027
5.00	0.261	0.027
4.70	0.261	0.027
4.40	0.279	0.009
4.20	0.300	-0.012
4.10	0.315	-0.027
4.00	0.328	-0.040
3.70	0.366	-0.078
3.40	0.386	-0.098
3.20	0.386	-0.098
3.10	0.386	-0.098
3.00	0.386	-0.098
2.70	0.385	-0.097
2.40	0.386	-0.098
2.20	0.386	-0.098
2.10	0.386	-0.098
2.00	0.386	-0.098

Table-3.17

Ni (II)- 2-Chlorobenzoic Acid-NTA System		
Ni(II)	$= 1 \times 10^{-3}\text{M}$	
2-Chlorobenzoic Acid	$= 1 \times 10^{-2}\text{M}$	Blank (A_0)= 0.445
$-\log[\text{NTA}]$	Absorbance (A)	Absorbance Difference ($A_0 - A$)
6.00	0.428	0.017
5.00	0.427	0.018
4.70	0.428	0.017
4.40	0.428	0.017
4.20	0.428	0.017
4.10	0.450	-0.005
4.00	0.469	-0.024
3.70	0.528	-0.083
3.40	0.582	-0.137
3.20	0.581	-0.136
3.10	0.582	-0.137
3.00	0.582	-0.137
2.70	0.582	-0.137
2.40	0.581	-0.136
2.20	0.582	-0.137
2.10	0.582	-0.137
2.00	0.582	-0.137

Table-3.18

Co (II) - 2-Chlorobenzoic Acid-NTA System		
Co(II)	= $1 \times 10^{-3}\text{M}$	
2-Chlorobenzoic Acid	= $1 \times 10^{-2}\text{M}$	Blank (A_0)= 0.365
-log[NTA]	Absorbance (A)	Absorbance Difference (A_0-A)
6.00	0.349	0.016
5.00	0.348	0.017
4.70	0.349	0.016
4.40	0.349	0.016
4.20	0.349	0.016
4.10	0.349	0.016
4.00	0.367	-0.002
3.70	0.413	-0.048
3.40	0.461	0.096
3.20	0.494	-0.129
3.10	0.501	-0.136
3.00	0.501	-0.136
2.70	0.500	-0.135
2.40	0.501	-0.136
2.20	0.501	-0.136
2.10	0.501	-0.136
2.00	0.501	-0.136

SECTION -III (C)

METAL-4-HYDROXYBENZOIC ACID-NTA SYSTEMS

Table-3.19

Fe(III) - 4-Hydroxybenzoic Acid-NTA System		
Fe(III)	$= 1 \times 10^{-4}\text{M}$	
4-Hydroxybenzoic Acid	$= 1 \times 10^{-3}\text{M}$	Blank (A_0) = 0.348
$-\log[\text{NTA}]$	Absorbance (A)	Absorbance Difference ($A_0 - A$)
6.00	0.324	0.024
5.00	0.324	0.024
4.70	0.325	0.023
4.40	0.324	0.024
4.20	0.325	0.023
4.10	0.324	0.024
4.00	0.324	0.024
3.70	0.324	0.024
3.40	0.346	0.002
3.20	0.361	-0.013
3.10	0.368	-0.020
3.00	0.376	-0.028
2.70	0.398	-0.050
2.40	0.412	-0.064
2.20	0.412	-0.064
2.10	0.412	-0.064
2.00	0.412	-0.064

Table-3.20

Cu(II) - 4-Hydroxybenzoic Acid-NTA System		
Cu(II)	= $1 \times 10^{-3}\text{M}$	
4-Hydroxybenzoic Acid	= $1 \times 10^{-2}\text{M}$	Blank (A_0) = 0.288
$-\log[\text{NTA}]$	Absorbance (A)	Absorbance Difference ($A_0 - A$)
6.00	0.265	0.023
5.00	0.265	0.023
4.70	0.266	0.022
4.40	0.265	0.023
4.20	0.266	0.022
4.10	0.265	0.023
4.00	0.265	0.023
3.70	0.265	0.023
3.40	0.290	-0.002
3.20	0.309	-0.021
3.10	0.318	-0.030
3.00	0.329	-0.041
2.70	0.359	-0.071
2.40	0.375	-0.087
2.20	0.375	-0.087
2.10	0.375	-0.087
2.00	0.375	-0.087

Table-3.21

Ni(II) - 4-Hydroxybenzoic Acid-NTA System Ni(II) = $1 \times 10^{-3}\text{M}$ 4-Hydroxybenzoic Acid = $1 \times 10^{-2}\text{M}$ Blank (A_0) = 0.455		
-log[NTA]	Absorbance (A)	Absorbance Difference ($A_0 - A$)
6.00	0.442	0.013
5.00	0.443	0.012
4.70	0.442	0.013
4.40	0.442	0.013
4.20	0.442	0.013
4.10	0.442	0.013
4.00	0.442	0.013
3.70	0.442	0.013
3.40	0.459	-0.004
3.20	0.488	-0.033
3.10	0.502	-0.047
3.00	0.518	-0.063
2.70	0.563	-0.108
2.40	0.588	-0.133
2.20	0.588	-0.133
2.10	0.588	-0.133
2.00	0.588	-0.133

Table-3.22

Co(II) - 4-Hydroxybenzoic Acid-NTA System		
Co(II)	$= 1 \times 10^{-3}\text{M}$	
4-Hydroxybenzoic Acid	$= 1 \times 10^{-2}\text{M}$	Blank (A_0) = 0.365
$-\log[\text{NTA}]$	Absorbance (A)	Absorbance Difference ($A_0 - A$)
6.00	0.353	0.012
5.00	0.352	0.013
4.70	0.353	0.012
4.40	0.353	0.012
4.20	0.352	0.013
4.10	0.353	0.012
4.00	0.353	0.012
3.70	0.353	0.012
3.40	0.353	0.012
3.20	0.375	-0.010
3.10	0.395	-0.030
3.00	0.409	-0.044
2.70	0.454	-0.089
2.40	0.497	-0.132
2.20	0.497	-0.132
2.10	0.497	-0.132
2.00	0.497	-0.132

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CHAPTER - IV

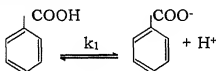
RESULT & DISCUSSION

RESULT AND DISCUSSION

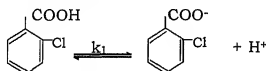
PREFATORY NOTE

The work described in the thesis comprises the study of binary complexes of Fe(III), Cu(II), Ni(II) and Co(II) with several acids viz. Benzoic Acid, 2-Chlorobenzoic Acid and 4-Hydroxybenzoic Acid and their ternary complexation using NTA as secondary ligand. The dissociation of these ligands depend upon the hydrogen ion concentration of the solution. The ligands deprotonates to different extent and their deprotonation may be represented as :

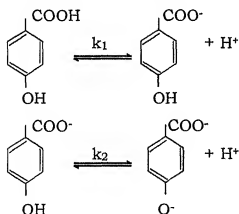
Benzoic Acid



2- Chlorobenzoic Acid



4- Hydroxybenzoic Acid



In the present work the dissociation constant of the liganding acids were taken from literature (9) which are given as :

Dissociation constant of Benzoic acid, $k_1 = 4.00$

Dissociation constant of 2-Chlorobenzoic Acid, $k_1 = 2.92$

Dissociation constant of 4-Hydroxybenzoic Acid, $k_1 = 4.58$, $k_2 = 9.46$.

BINARY METAL COMPLEXES

Ionic species of the various ligands viz Benzoic Acid, 2-Chlorobenzoic Acid and 4-Hydroxybenzoic Acid exist as fully deprotonated species and they form complexes, with the metal ions. The extent of complexation depends upon the availability of the ionic species and the stability constants of the resulting complexes. The metal ion is supposed to exhibit a change in its electrophoretic mobility when combines with the different ligands. The complexation of Fe(III), Cu(II), Ni(II) and Co(II) with Benzoic Acid, 2-Chlorobenzoic Acid and 4-Hydroxybenzoic Acid have been investigated in the presence of varying concentrations of liganding species.

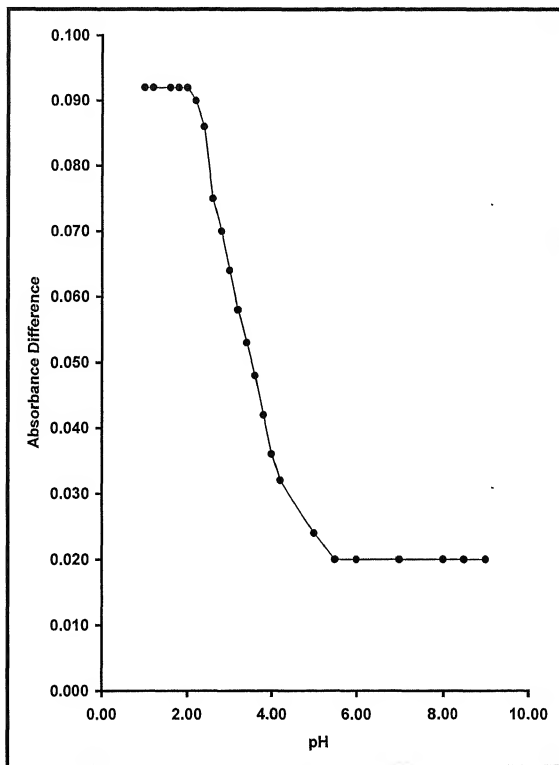
The observation on overall electrophoretic mobility (absorbance difference) of four metal ions viz. Fe(III), Cu(II), Ni(II) and Co(II) are recorded in tables (2.11 to 2.22). These observations reveal the variation of electrophoretic mobility of metal ion in solution with varying pH's of the background electrolyte which contains $1 \times 10^{-2} \text{M}$ ligand for Cu(II), Ni(II), Co(II) and $1 \times 10^{-3} \text{M}$ ligand for Fe(III).

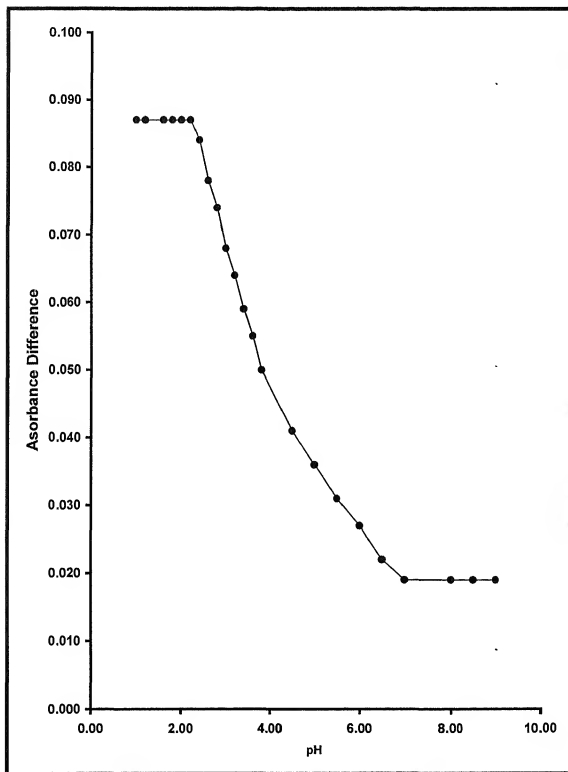
The increase of pH leads to the increase in concentration of deprotonated species of these acids. Chemical literature shows abundant evidence for L^- species of acids viz. Benzoic Acid, 2-Chlorobenzoic Acid and HL^- & L^{2-} species of 4-Hydroxybenzoic Acid to be the most effective potential liganding species.

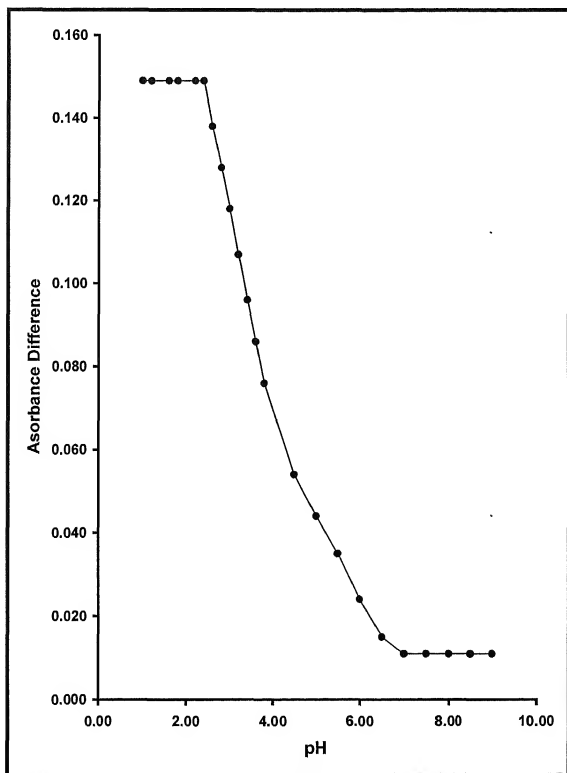
The graphs plotted between absorbance difference and pH's of the solution mixture which are shown in figure (4.11 to 4.22) give two plateaus with Fe(III), Cu(II), Ni(II) and Co(II).

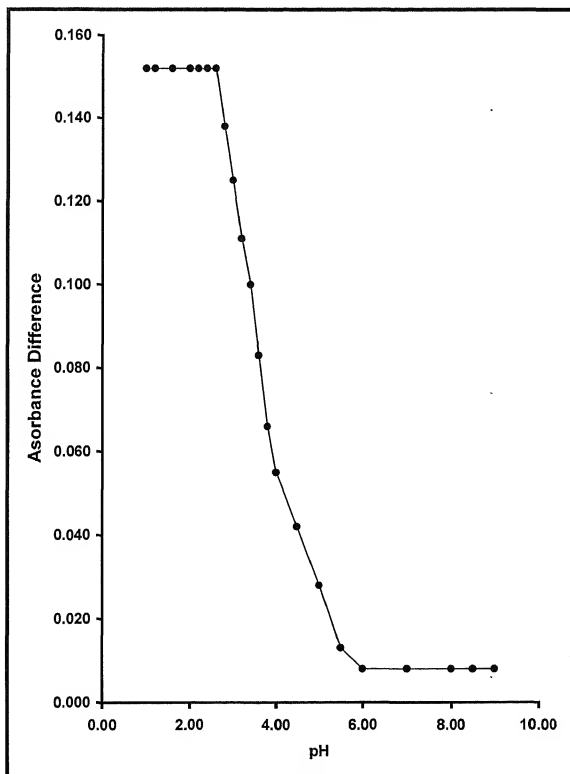
A plateau is an indication of a pH range over which mobility is practically constant. This could be possible only when a particular complex species is formed in abundance. Thus each plateau indicates the formation of certain complex species.

The first plateau in the beginning at low pH is ascribed to the uncomplexed metal ion. Here the concentration of highly protonated species of the ligand are obviously maximum. Beyond this plateau as the hydrogen ion concentration increases all ligands are increasingly deprotonated to produce HL^- , L^- and L^{2-} anionic species for different ligands. This has also been confirmed from the observations of other workers (37, 14, 20). In this region complexation of the metal ions takes place with these anionic species to produce complexes which give second plateau in the curve. This plateau corresponds to the formation of 1:1 metal complexes with each ligand. The lower positive mobility of second plateau than that of first plateau supports the formation of 1:1 positively charged complexes of the type MHL^+ and ML^+ . In case of benzoic acid and chlorobenzoic acid the ligand species is L^- and the complexes formed are ML^+ type, whereas in hydroxybenzoic acid the liganding species is HL^- type and forms MHL^+ complexes with the metal ion. Further increase in the pH beyond this plateau does not give any change in the mobility of the metal ions, indicating that ML_2 or $M(HL)_2$ type 1:2 complexes are not formed.

MOBILITY CURVE**Fe(III) - Benzoic Acid****Fig. 4.11**

MOBILITY CURVE**Cu(II) - Benzoic Acid****Fig. 4.12**

MOBILITY CURVE**Ni(II) - Benzoic Acid****Fig. 4.13**

MOBILITY CURVE**Co(II) - Benzoic Acid****Fig. 4.14**

MOBILITY CURVE

Fe(III) - 2-Chlorobenzoic Acid

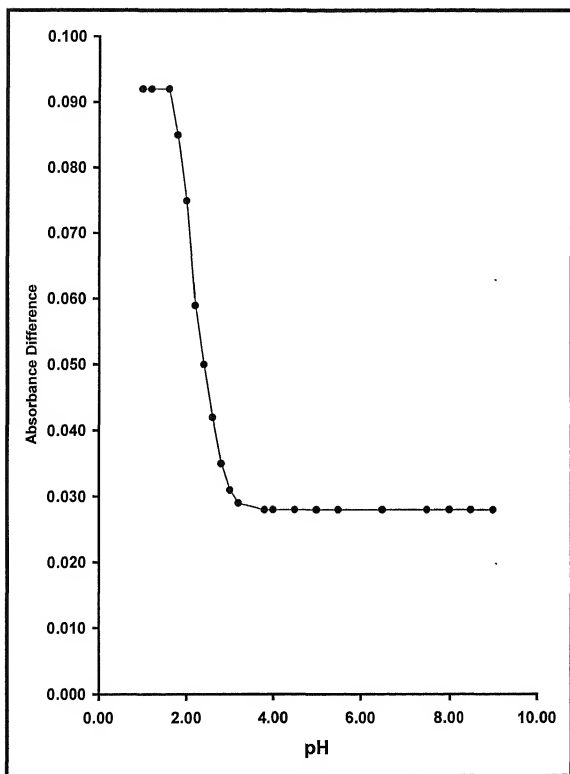


Fig. 4.15

MOBILITY CURVE

Cu(II) - 2-Chlorobenzoic Acid

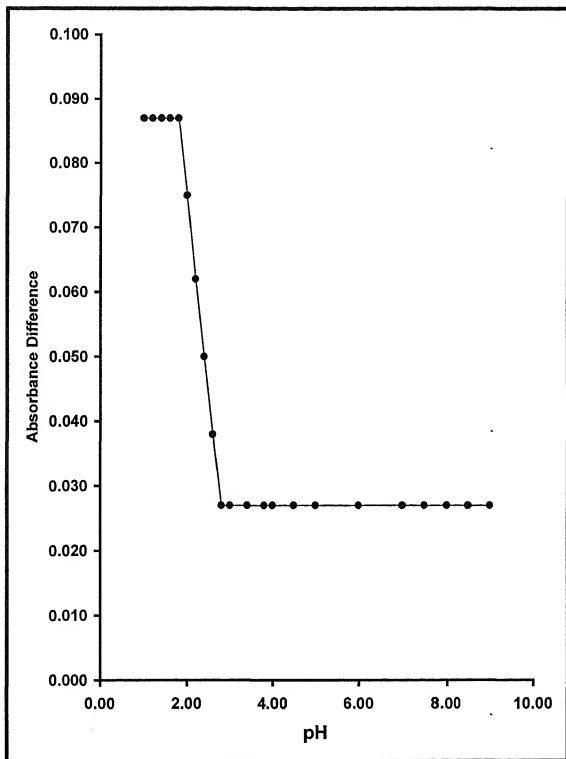


Fig. 4.16

MOBILITY CURVE

Ni(II) - 2-Chlorobenzoic Acid

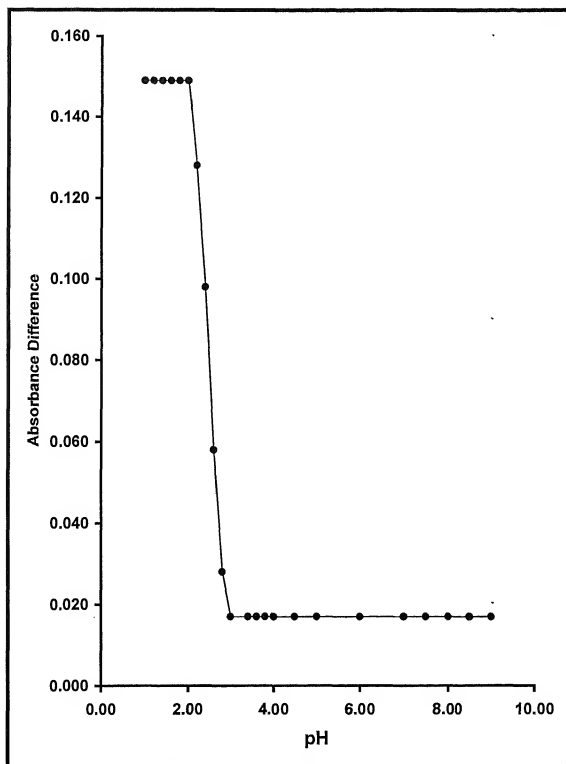


Fig. 4.17

MOBILITY CURVE

Co(II) - 2-Chlorobenzoic Acid

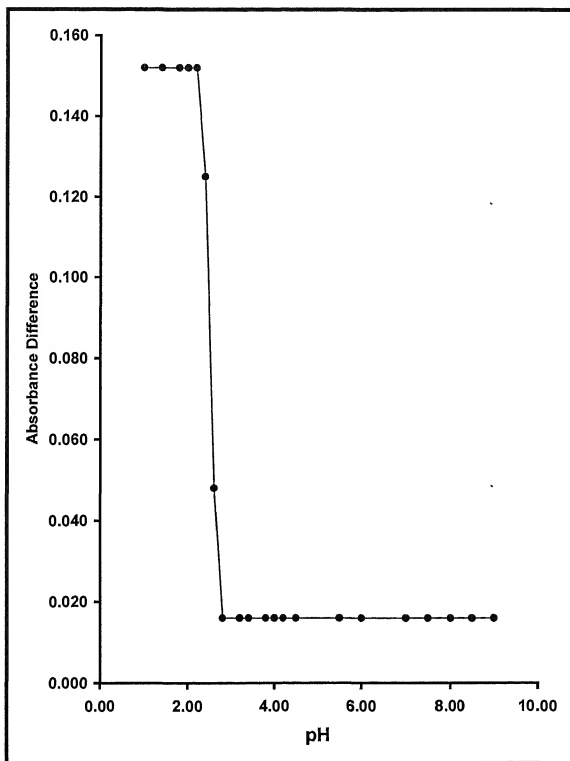


Fig. 4.18

MOBILITY CURVE

Fe(III) - 4-Hydroxybenzoic Acid

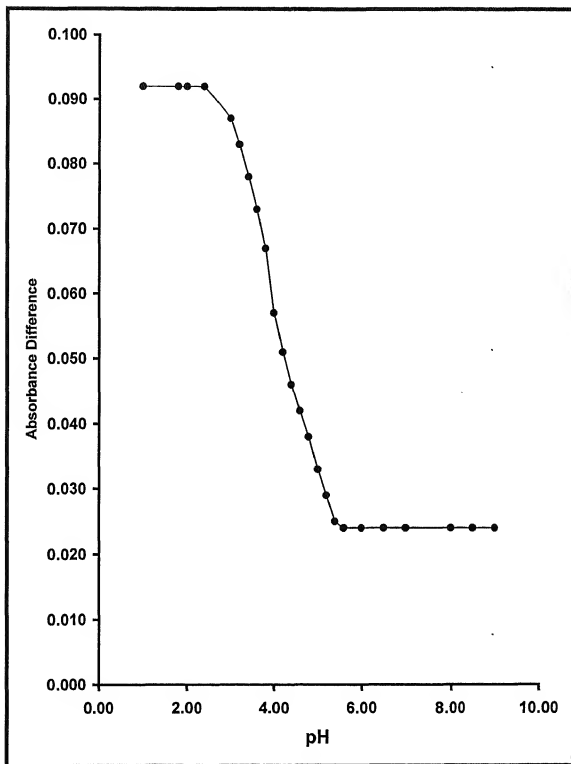


Fig. 4.19

MOBILITY CURVE

Cu(II) - 4-Hydroxybenzoic Acid

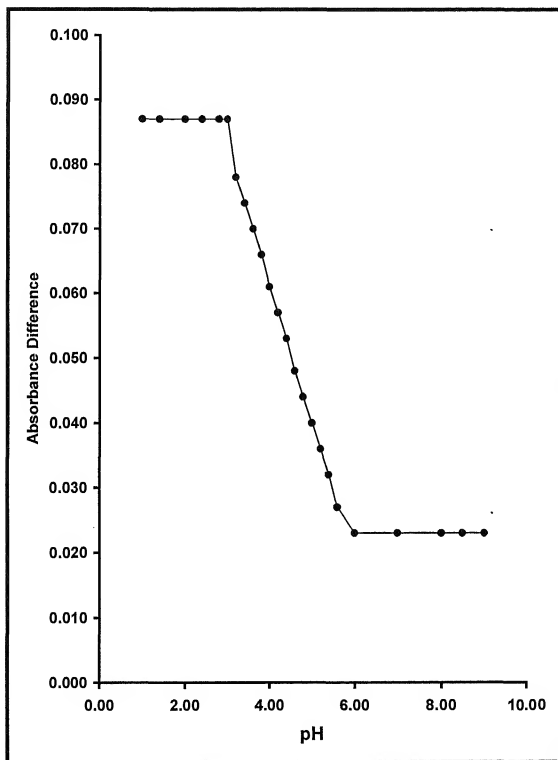
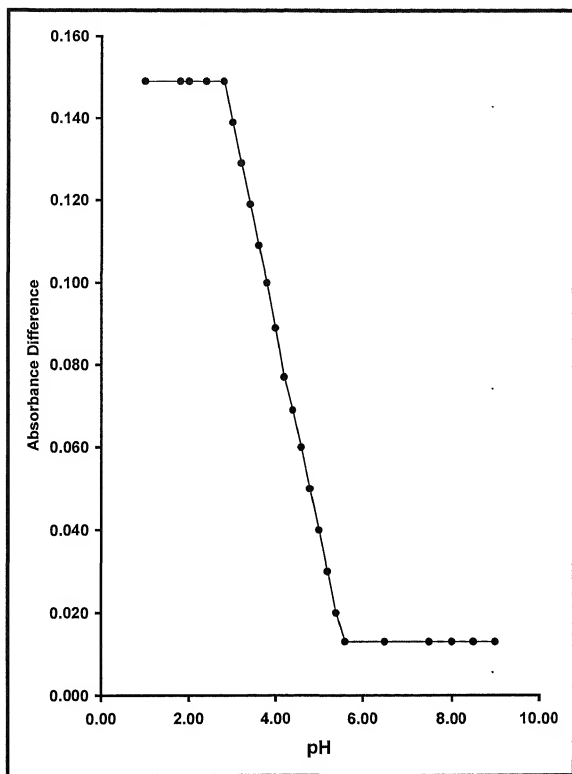


Fig. 4.20

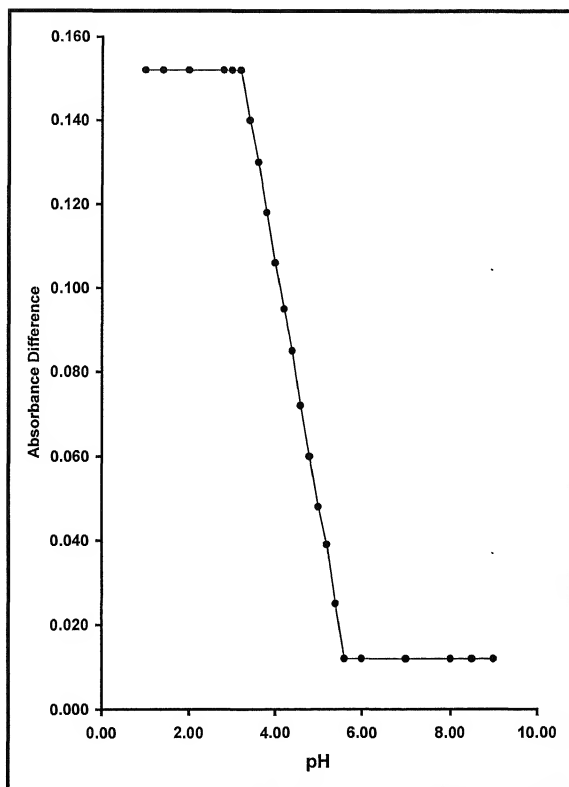
MOBILITY CURVE

Ni(II) - 4-Hydroxybenzoic Acid

**Fig. 4.21**

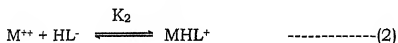
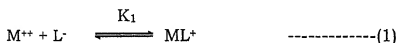
MOBILITY CURVE

Co(II) - 4-Hydroxybenzoic Acid

**Fig. 4.22**

CALCULATION OF STABILITY CONSTANTS OF BINARY COMPLEXES

For calculation of stability constants of the different complexes obtained with different ligands, the equation (6) of chapter I has been utilized. It is clear from the present work that complexes between metal ions and the ligands are of 1:1 composition. The deprotonated species HL, L (charges ignored) i.e. anion of the various ligands used, has been assumed to be the ligand for complexation with metal ions. The interaction of metals with ligands may be represented as



The relation between overall mobility of the metal complex species with the concentration of different anionic species of Benzoic Acid, 2-Chlorobenzoic Acid may be represented as :

$$U = \frac{u_M + u_{ML}K_1[L^-] + u_{ML_2}K_2[L^-]^2}{1 + K_1[L^-] + K_2[L^-]^2} \quad \text{-----}(3)$$

Whereas for 4-Hydroxybenzoic Acid it will as :

$$U = \frac{u_M + u_{MHL}K_1[HL^-] + u_{ML}K_2[L^-]}{1 + K_1[HL^-] + K_2[L^-]} \quad \text{-----}(4)$$

Where K_1 and K_2 are different stability constants of the metal ligand complexes and U 's are the mobilities of complex ionic species.

The curves have been plotted between absorbance difference and pH's of the reaction mixture which are shown in figures (4.11 to 4.22). As discussed earlier Fe(III), Cu(II), Ni(II) and Co(II) with all ligands show two plateaus. The first plateau corresponds to uncomplexed metal ion and the second plateau corresponds to the formation of monopositive complex. With the help of first two plateaus, the stability constant of the metal

complex can be calculated as indicated in eq. (1). The transition from first plateau to second plateau represents conversion of uncomplexed metal ion into monopositive metal complexes. Hence the mobility in the transitions range is actually the additive mobility of uncomplexed metal ion and monopositive metal complex weighed with their actual fractions modified as:

$$U = \frac{u_M + u_{ML}K_1[L^-]}{1 + K_1[L^-]} \quad \text{----- (5)}$$

or

$$U = \frac{u_M + u_{MHL}K_1[HL^-]}{1 + K_1[HL^-]} \quad \text{----- (6)}$$

Obviously the overall mobility 'U' will be equal to the mean of the mobility of uncomplexed metal ion u_M and of monopositive complex cation u_{ML+} or u_{MHL+} . i.e. $U = u_M + (u_{ML+} \text{ or } u_{MHL+})/2$ provided $K[L]$ or $K[HL] = 1$. With the help of dissociation constants of acids the concentration of various anionic species have been calculated at particular pH. The reciprocal of the concentration gives stability constant.

The calculated values of stability constants K , of Fe(III), Cu(II), Ni(II) and Co(II) complexes with Benzoic Acid, 2-Chlorobenzoic Acid and 4-Hydroxybenzoic Acid are given in Table-1.

STABILITY CONSANTS OF BINARY COMPLEXES

TABLE-1

(Temperature = 25°C, Ionic Strength=0.1M)

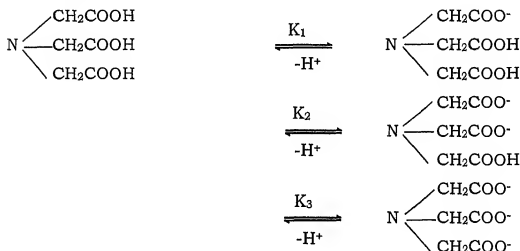
METAL ION	CALCULATED Log K VALUES		
	Benzoic Acid	2-Chlorobenzoic Acid	4-Hydroxybenzoic Acid
Fe (III)	3.65	3.84	3.57
Cu(II)	2.51	2.71	2.46
Ni(II)	2.47	2.64	2.43
Co(II)	2.44	2.60	2.40

TERNARY METAL COMPLEXES

COMPLEXATION WITH NTA

Nitrilotriacetic Acid is an excellent polydentate ligand. In this chapter Nitrilotriacetic acid is used as a ligand with mixed complexation reactions. The NTA is used as a secondary ligand. Its dissociation constants and its complexes with metal ions are prerequisite. Much works have been done in the past on this aspect and many reviews exist (1, 8, 22, 23, 34).

NTA (Nitrilotriacetic acid) dissociates as follows :



NTA on ionization gives ultimately triply charged anion which is a powerful tridentates (38) or tetradentate ligand.

The work of D. Mehrotra (15), D. Gupta (6), U. Mishra (16) and A.K. Nathaniel (19) depicts the formation of complexes of the metal ions with NTA.

Observations on overall mobility of metal ions in the presence of NTA at different pH values has also been determined electrophoretically in these laboratories by Yadav et-al (26, 27, 28, 29, 30, 31, 32, 39) at 35°C.

Coordination of different metal ions with this ligand have been widely investigated by several workers (3, 7, 9, 11, 12, 17, 24). In the literature the dissociation constants of NTA have been reported to be $k_1 = 1.80$, $k_2 = 2.48$ and $k_3 = 9.65$.

BINARY COMPLEXES OF NTA

Each bivalent metal ion gives two plateaus with NTA and the mobility of the last plateau is negative. So it is concluded that the bivalent metal-ions form 1:1 metal-NTA complexes, which is in confirmation of the finding of other workers (5, 10). With the increase in pH the absorbance difference in the positive mobility range crosses the zero mobility level and continues to decrease till it becomes constant giving the second plateau in the negative range of the mobility. The decrease in absorbance difference is due to progressive complexation of metal ions with triply charged anionic species of NTA, till the last plateau is obtained which is obviously an anionic species and is in 1:1 composition. Any further increase in pH does not change the nature of the curve suggesting no formation of any other new complex.

The experiments for binary complexes of Cu(II)-NTA, Ni(II)-NTA, Co(II)-NTA and Zn(II)-NTA have been carried out by Singh, M.P. (25) and by Shagufta Zamani (40) and the same work has been repeated by Sameena (21) along with Fe(III)-NTA complexes.

To avoid the repetition of work the related graphs and stability constants of M-NTA complexes have been taken from the above mentioned doctoral thesis, whenever it is necessary for making comparison.

TERNARY METAL COMPLEXES WITH NTA

The present work included the study of the ternary complexes of Fe(III), Cu(II), Ni(II) and Co(II) using Benzoic Acid, 2-Chlorobenzoic Acid, 4-Hydroxybenzoic Acid as a primary ligand and NTA as a secondary ligand. The study of these complexes have been carried out in presence of Benzoic Acid/2-Chlorobenzoic Acid/4-Hydroxybenzoic Acid with progressive addition of secondary ligand NTA, from $1 \times 10^{-6} \text{M}$ to $1 \times 10^{-2} \text{M}$ at a fixed pH 7.0. The observations are given in table (3.11 to 3.22) and graphically represented in figure (5.11 to 5.22). These figures clearly show two plateau's, the first plateau corresponds to binary M-Benzoic Acid/2-Chlorobenzoic Acid/4-Hydroxybenzoic Acid complexes whereas, second plateau corresponds to the formation of new complex.

The new complex may be mixed complex of the type M-L-NTA, or pure M-NTA complex. But with the help of related graph of M-NTA complexes, it was found that the absorbance difference in case of new complex is not identical to M-NTA pure complex. So it is interpreted that it is a mixed complex. Further this ternary complex has greater negative mobility than that of binary complex. Hence these observations confirm the formation of mixed M-L-NTA complex.

MOBILITY CURVE

Fe(III) - Benzoic Acid-NTA System

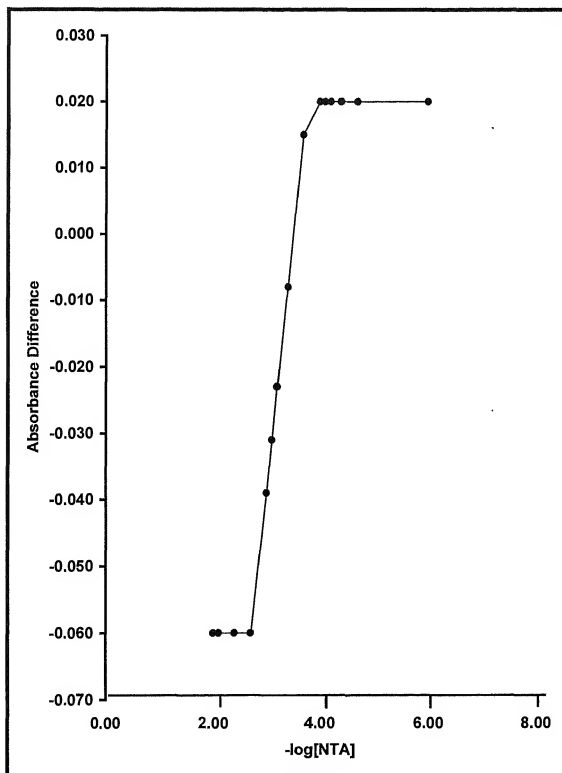


Fig. 5.11

MOBILITY CURVE

Cu(II) - Benzoic Acid-NTA System

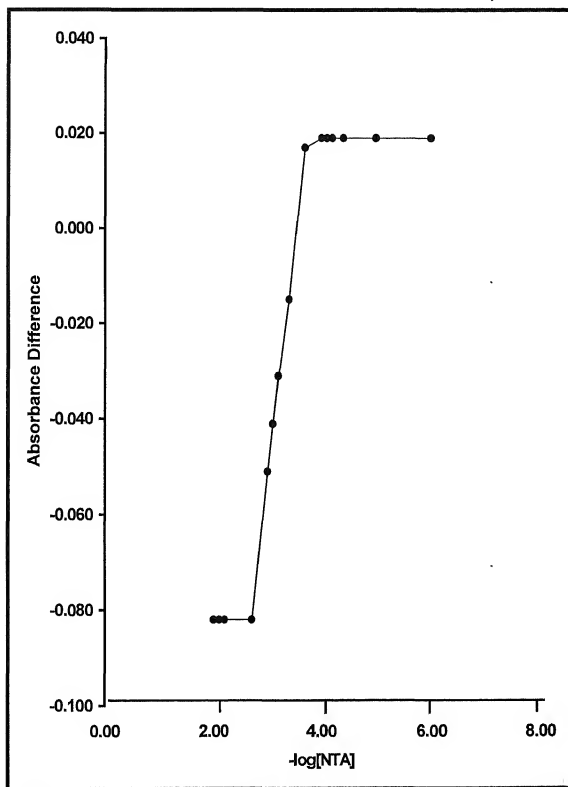


Fig. 5.12

MOBILITY CURVE

Ni(II) - Benzoic Acid-NTA System

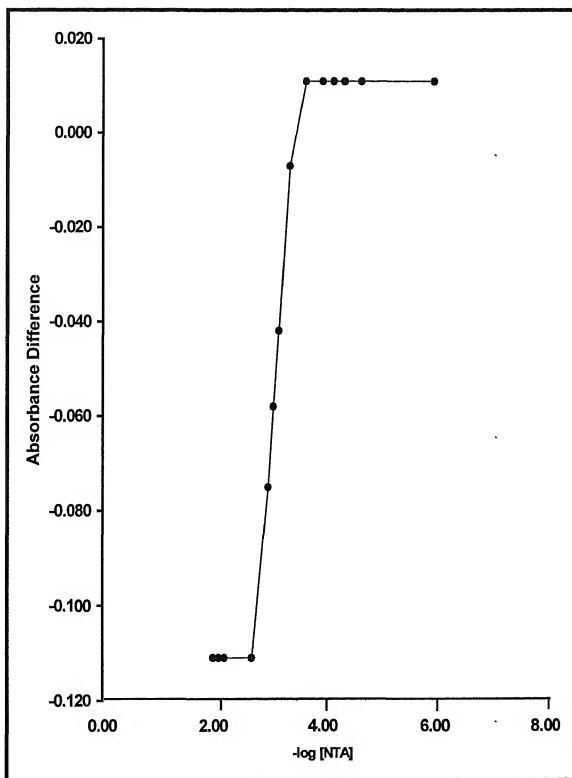


Fig. 5.13

MOBILITY CURVE

Co(II) - Benzoic Acid-NTA System

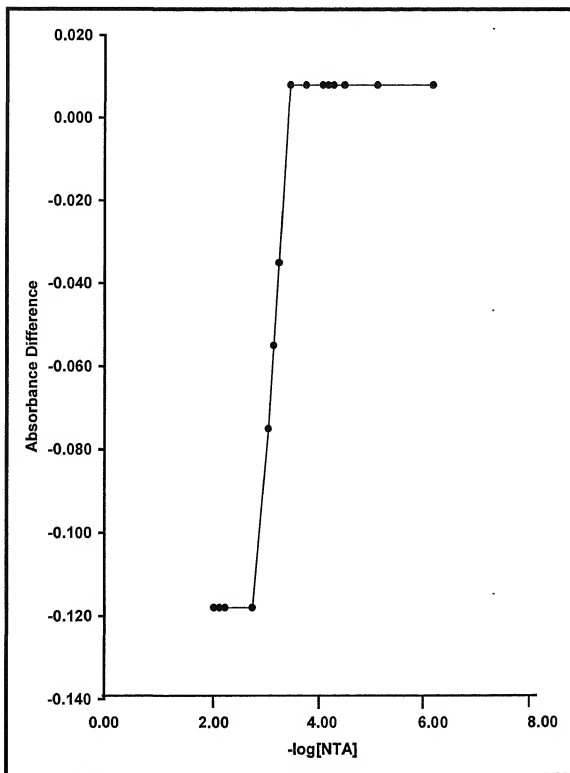
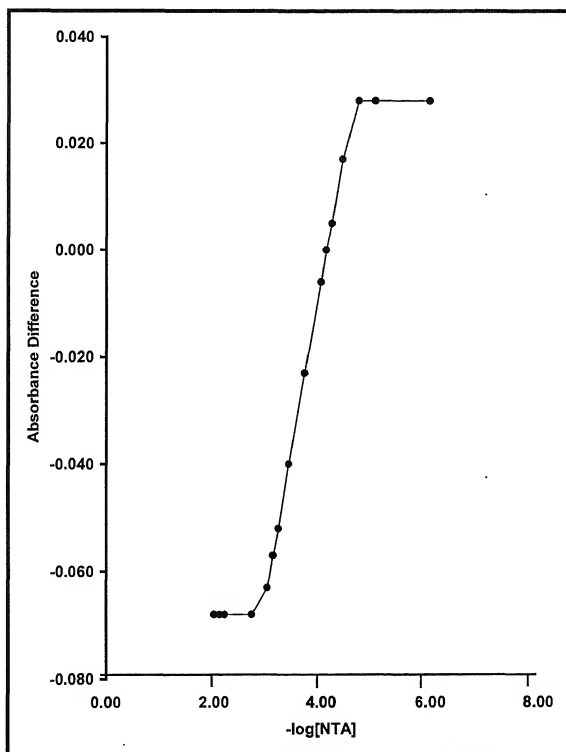


Fig. 5.14

MOBILITY CURVE**Fe(III) - 2-Chlorobenzoic Acid-NTA System****Fig. 5.15**

MOBILITY CURVE

Cu(II) - 2-Chlorobenzoic Acid-NTA System

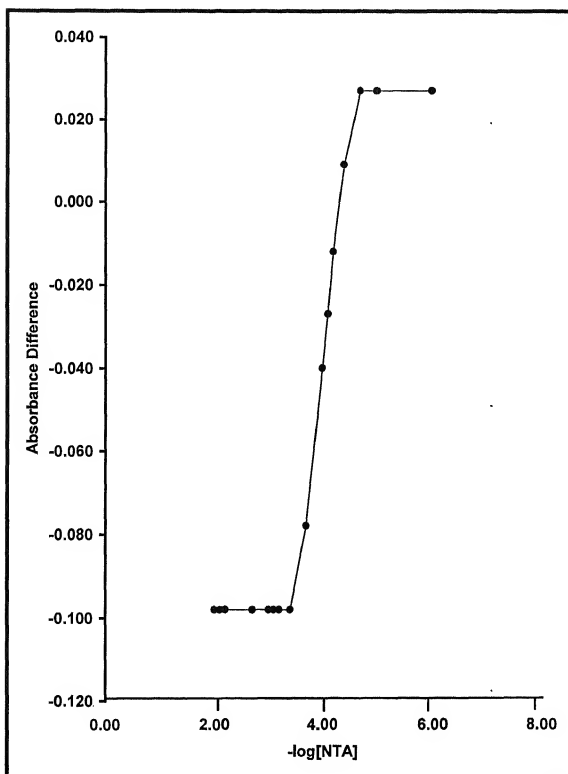


Fig. 5.16

MOBILITY CURVE

Ni(II) - 2-Chlorobenzoic Acid-NTA System

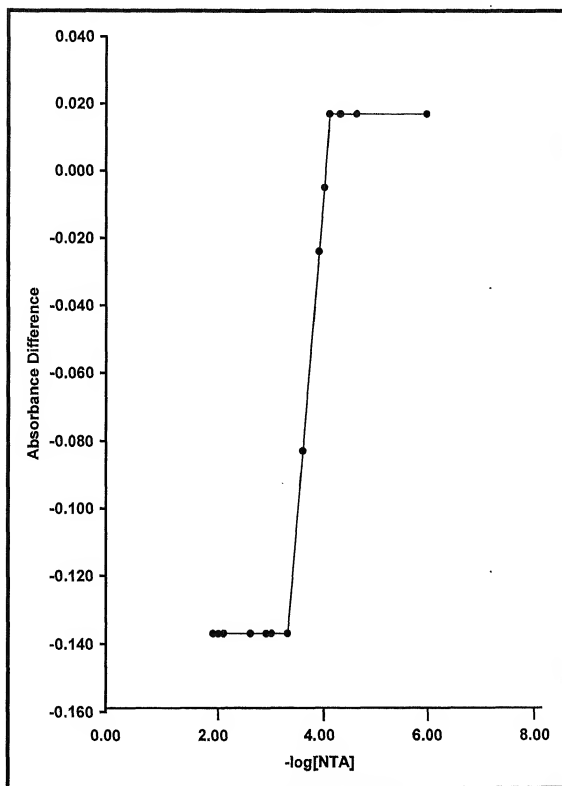


Fig. 5.17

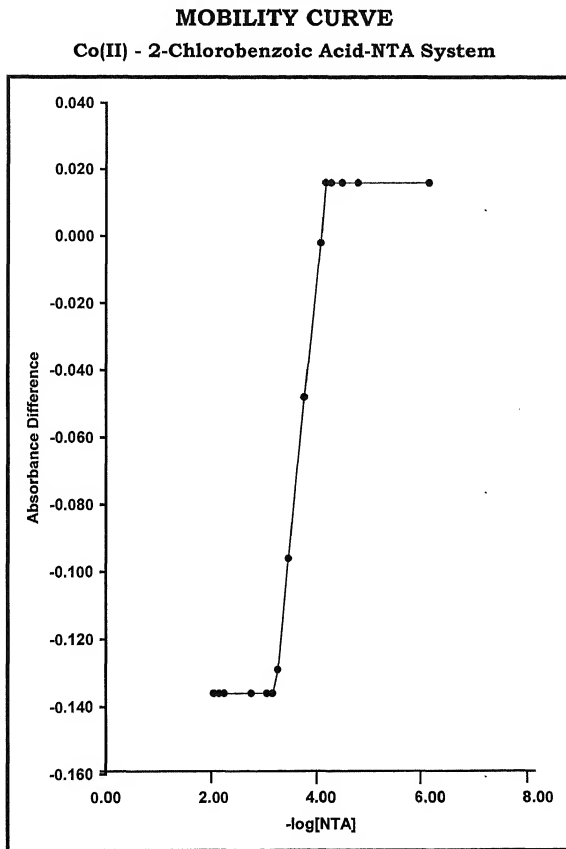
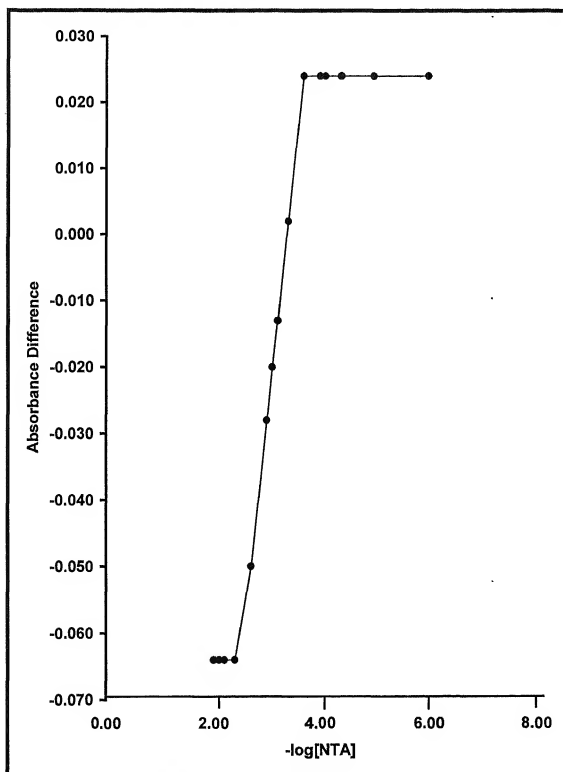
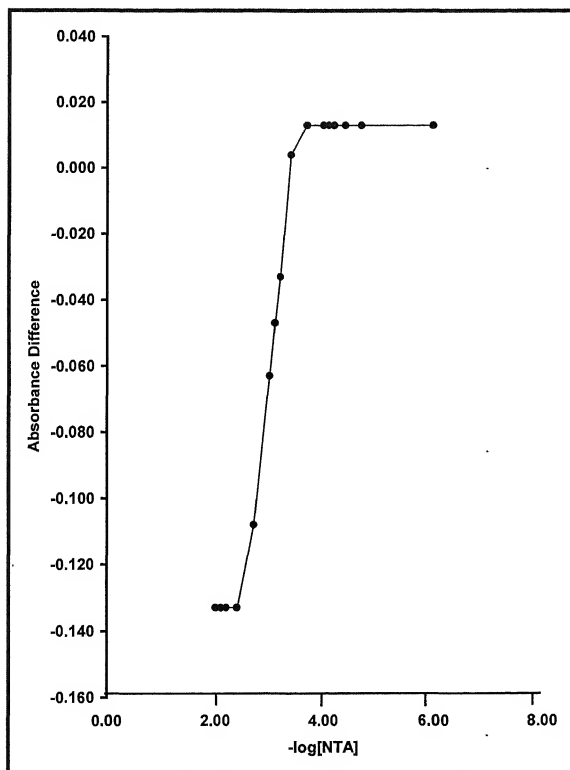
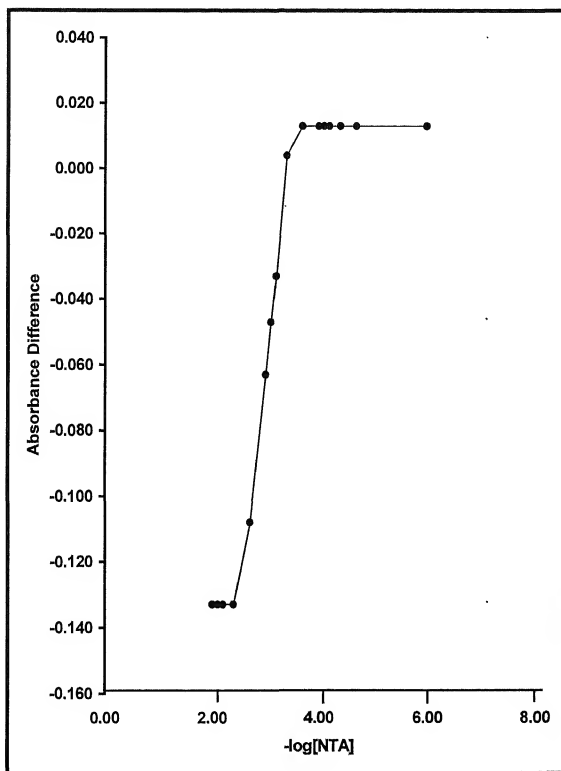
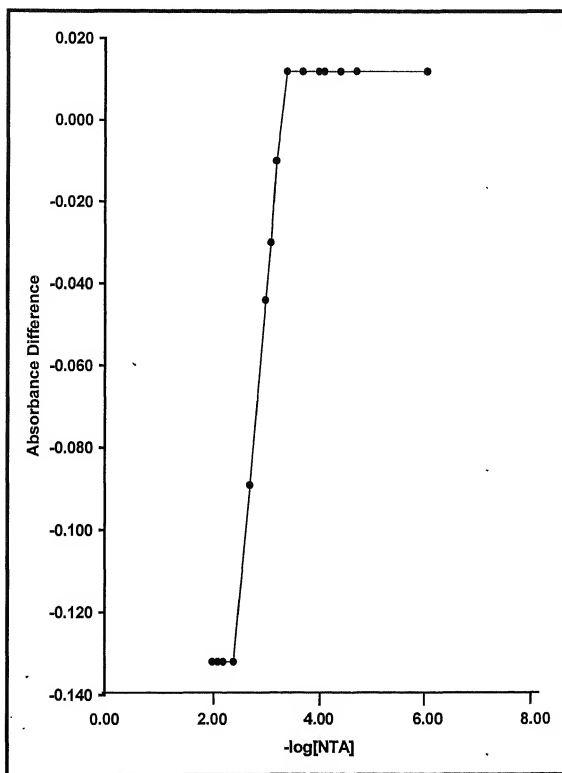


Fig. 5.18

MOBILITY CURVE**Fe(III) - 4-Hydroxybenzoic Acid-NTA System****Fig. 5.19**

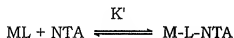
MOBILITY CURVE**Cu(II) - 4-Hydroxybenzoic Acid-NTA System****Fig. 5.20**

MOBILITY CURVE**Ni(II) - 4-Hydroxybenzoic Acid-NTA System****Fig. 5.21**

MOBILITY CURVE**Co(II) - 4-Hydroxybenzoic Acid-NTA System****Fig. 5.22**

CALCULATION OF STABILITY CONSTANTS OF TERNARY COMPLEXES

The transformation of M-L complex into M-L-NTA complex can be represented as



Where K' represents the stability constant of M-L-NTA complexes.

For M-L-NTA complexes the stability constant K' can be represented as :

$$K' = \frac{[M-L-NTA]}{[ML][NTA]}$$

Hence, the overall mobility ('U') is given by

$$'U' = u_0 f_{ML} + u_1 f_{M-L-NTA} \text{ (for M-L-NTA complexes)}$$

Where u_0 , u_1 and f_{ML} , $f_{M-L-NTA}$ are the mobilities and the mole fractions of M-L and M-L-NTA complexes, respectively. Substituting the values of mole fractions, the overall mobility is given by

$$'U' = \frac{u_0 + u_1 K' [L']}{1 + K' [L']}$$

From the figures concentration of NTA at which overall mobility is mean of the mobilities of the two plateaus is determined. The concentration of NTA anion at pH 7.0 for this NTA concentration is calculated, K' is obviously equal to $1/[NTA]$. All these values of K' are given in Table-2 which clearly indicates the superior coordinating power of NTA anion to other carboxylic acid species.

STABILITY CONSTANTS OF TERNARY COMPLEXES**TABLE-2**

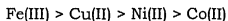
(Temperature = 25°C, Ionic Strength=0.1M)

METAL ION	CALCULATED Log K' VALUES		
	Benzoic Acid	2-Chlorobenzoic Acid	4-Hydroxybenzoic Acid
Fe (III)	6.69	5.85	5.70
Cu(II)	6.65	5.80	5.65
Ni(II)	6.45	5.75	5.55
Co(II)	6.20	5.70	5.50

GENERAL COMPARISON

Stability constants of the so formed complexes of the three ligands viz.: Benzoic Acid, 2-Chlorobenzoic Acid and 4-Hydroxybenzoic Acid should be examined in context of the structure of these acids and nature of the central metal ion as well. The differential behaviour of these three ligands is mainly accountable by their structural differences and presence of different groups in the chain.

The foregoing tables bear out the stability constants of different metal complexes determined by us. As regards the role of metal ions in complexation with these ligands, one perceives gradation in their complexing capacities in the order



The above order is in accordance with "Irving and Williams Natural Order of Stability". Irving and Williams realized the significance of charge on the metal ions in complexation with the ligand and obtained the sequence $\text{Mn(II)} > \text{Fe(II)} > \text{Cu(II)} > \text{Ni(II)} > \text{Co(II)}$. Their rule regarding the effectiveness of metal ion is based on their ionic potential (Ze^2/r). It may be remarked that this rule is by far the most satisfactory working rule for the transition metals in the bivalent state. However it has its limitations in as much as it does not take into account the specific spatial arrangement of co-ordinating ligand around the central metal ions. The remarkable stability of Ca(II) with ethylene diamine tetraacetic acid and Ni(II) with dimethyl glyoxime is a clear example of the view point (18). The nature of the ligand, nature of metal ion and nature of the metal-ligand bond (size and nature of the chelate ring, base strength of the ligand donor group, steric effect, resonance effect, stabilization energy, electrostatic attraction) are the factors which govern the stability. Hence according to Irving and Williams order and extension of this rule by Basolo and Pearson (2), the order of stability constants for bivalent metal ions is $\text{Cu(II)} > \text{Ni(II)} > \text{Co(II)}$,

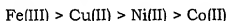
which is same order as in our calculated values. The higher stability constants of Fe(III) complexes with those of bivalent metal ions can be attributed to its higher charge.

The complexing capacity of the metal complexes with reference to ligands is found to be in the following order.

Metal-2-Chlorobenzoic Acid complexes > Metal-Benzoic Acid complexes > Metal-4-Hydroxybenzoic Acid complexes.

This can be explained on the basis of the basic nature of the ligands. The more basic ligand the stronger will be the complex.

The stability constants of ternary complexes also shows that the metal ions can be arranged in the following order in accordance with their decreasing complexing behaviour.



The order is also in accordance with the Irving William's Order.

The stability constants of the ternary complexes with reference to ligands are found to be in the following order.

Metal-Chlorobenzoic Acid-NTA complexes > Metal-Benzoic Acid - NTA complexes > Metal-4-Hydroxybenzoic Acid-NTA complexes.

The above order is again to be understood in terms of basicity of the ligands. All the ligands used in the present investigation are bidentate and NTA is a tetradentate ligand. The superiority of NTA over the other ligands lies in possession of two additional coordinative sites in a single moiety.

The stability constant can be interpreted as a measure of strength of coordination linkages in a complex. It is therefore inferred that the coordinating tendency of a ligand decreases with higher states of aggregation. In other words metal progressively loses its tendency of linkage with a ligand on progressive filling of vacant orbitals. This conclusion is of universal validity as evidenced in chemical literature

(2, 36,). The above conclusion is also true in the realm of mixed complexes.

Thus Ionophoretic technique used in the above studies proved to be very useful in studying the stepwise complexation in solution. The special electrophoretic tube (33) which has been designed for this work yields better results after standardization. Its application in the study of ternary complexes is an unique advancement in the field of coordination chemistry.

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